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VOL. V.

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DICTIONARY OF CHEMISTRY.

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A DICTIONARY

OF

CHEMISTRY

AND THE

ALLIED BRANCHES OF OTHER SCIENCES.

BY

HENRY WATTS, B.A., F.R.S., F.C.S.

EDITOR OF
'THE JOURNAL OF THE CHEMICAL SOCIETY.'

ASSISTED BY EMINENT CONTRIBUTORS.

IN FIVE VOLUMES.

VOL. V.

QUADRANTOXIDE—ZYMURGY.

LONDON:
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1868.

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PREFACE

TO

THE FIFTH VOLUME.

THE NINE YEARS which have elapsed since this work was commenced have witnessed important changes in the modes of viewing and representing the constitution of chemical compounds. The old system of notation, founded on the dualistic theory of chemical combination, and the atomic weights adopted in Gmelin's Handbook and other standard works of older date, may now be regarded as belonging to the past; and even the new system introduced by Gerhardt has undergone considerable modification, the atomic weights which that chemist assigned to many of the metals having been doubled, and his system of typical representation having been developed into the modern theory of atomicity. These changes and developements are explained in the article CLASSIFICATION by Professor G. C. Foster, and the articles ATOMIC WEIGHTS, and METALS, ATOMIC WEIGHTS AND CLASSIFICATION OF, by Dr. Odling. The smaller atomic weights of many of the metals ($Ba=68{\cdot}7$; $Hg = 100$; $Zn = 32{\cdot}5$, &c.) having been adopted in the earlier part of the Dictionary, it was thought advisable, in first introducing the larger ones, to distinguish them by doubled symbols ($Bba = 137$, $Hhg = 200$, &c.); but in the latter part of the work these double symbols, which are rather clumsy, have been abandoned, and the ordinary symbols used, with accents or dashes, when necessary, to indicate the equivalent value.

In bringing the Dictionary to a conclusion I have to regret that it is in some respects less complete than I could wish. Although it has extended considerably beyond the limits originally contemplated, the space has still been found too narrow for the adequate treatment of many important subjects. I have however endeavoured to give some notice of every compound discovered up to the time of the publication of each Part of the

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work, and where full description was impossible, reference is given to the original sources of information. The earlier volumes are necessarily somewhat behind the present state of knowledge, but should the work meet with the success for which we hope, this deficiency may perhaps be made good by a Supplement.

In conclusion I have to tender my best thanks to those gentlemen who have enriched the work by their valuable contributions. Several of these articles have taken rank as classical treatises on their respective subjects, and to them the work will be in a great measure indebted for such success as it may attain.

HENRY WATTS.

LONDON: *May*, 1868.

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⁂ Articles communicated by the several contributors are signed with their initals; articles taken from URE's *Dictionary of Chemistry* (fourth edition, 1831) are signed with the letter U; those which have no signature are by the Editor.

DICTIONARY OF CHEMISTRY.

Q

QUADRANTOXIDE. A term applied by H. Rose to oxides containing 4 atoms of metal to 1 atom of oxygen, such as suboxide of silver Ag^4O: better called *tetrametallic oxides* (see Oxides, iv. 304).

QUADRI and **QUADRO.** Prefixes synonymous with Tetra: *e.g.* $SnCl^4$ = Quadrichloride or Tetrachloride of tin.

QUARTZ. Native crystalline anhydrous silica, SiO^2, occurring either in distinct crystals, often of large size, or in crystalline aggregates, or massive.

The crystals belong to the hexagonal system, being six-sided prisms with pyramidal summits, made up of the two opposite rhombohedrons, $+R$ and $-R$, with the corresponding prism ∞R; hemihedral or tetartohedral, exhibiting the modifications described under Crystallography (ii. 139—143). For R, the principal axis = 1·100. Angle $R : R$ (terminal) = 94° 15′. For the hexagonal pyramid, the angle of the terminal edges = 133° 4′; of the lateral edges = 103° 34′. Cleavage very imperfect, parallel to R and ∞R. Twins are of frequent occurrence, the face of composition being either the basal plane, oR, or a plane truncating the pyramidal edge, or the face R. The two crystals compounded parallel to oR, sometimes penetrate one another very irregularly, while the external planes are regular and even (Dana, ii. 146). Distorted crystals also occur, sometimes curved, as in figure 355 (ii. 166).

Hardness = 7. Specific gravity = 2·5—2·8; according to Beudant, = 2·6413—2·6541; according to Hauy, = 2·6701. Lustre vitreous, sometimes inclining to resinous. Colourless when pure (rock-crystal); but often exhibiting various shades of yellow, red, brown, green, blue, and black, from admixture of oxide of iron and other metallic oxides. Streak, of the pure varieties, white; of the impure, often the same as the colour, but much paler. Transparent to opaque. Fracture perfect conchoïdal to subconchoïdal. Tough; brittle; friable. Infusible alone before the blowpipe, but with carbonate of sodium it fuses readily, and with effervescence, to a transparent glass.

Quartz exhibits numerous varieties, arising from peculiar modes of formation and crystallisation, or from impurities. They may be divided into three groups—namely, the vitreous varieties, exhibiting the bright glassy lustre of broken quartz-crystals; the chalcedonic varieties, exhibiting the glistening subvitreous or waxy lustre and translucency of chalcedony; and the jaspery varieties, having the dull lustre and colours and the opacity of jasper. The varieties belonging to the second and third groups have been already described. (See Chalcedony, i. 844; Jasper, iii. 442; and the names of the several varieties.)

The vitreous group includes: α. *Rock-crystal*, or pure crystallised quartz. An asteriated variety contains whitish impurities or opaque particles, arranged along the diametral planes.—β. *Amethyst:* clear purple or bluish-white quartz-crystal, the colour being generally ascribed to a small percentage of oxide of manganese. According to Heintz, however, it is due to a compound containing iron and sodium.—γ. *Rose-quartz:* rose-red or pink; transparent or nearly so, with vitreous lustre; usually massive, and often much cracked. The colour is probably due to manganese, but is attributed by Fuchs to oxide of titanium, and by Berthier to organic matter.—δ. *False topaz:* a light-yellow pellucid variety of quartz-crystals, resembling yellow topaz, but distinguished therefrom by its crystalline form, and the absence of cleavage.—ε. *Smoky* *quartz* or *Cairngorm-stone* has a brownish smoky tint, sometimes pellucid.—ζ. *Milky quartz:* one of the most common varieties, massive, vitreous, with a milk-white colour. Sometimes it has a greasy lustre, and is then called *greasy quartz*.—η. *Prase* is a leek-green variety of massive quartz.—θ. *Aventurin quartz* is minutely spangled throughout the mass with yellow scales. It is usually translucent, and of a grey, brown, or reddish-brown colour.—ι. *Siderite:* a blue variety from Golling, near Saltzburg.—κ. *Ferruginous quartz* is of an opaque red, brownish-red, or ochre-yellow colour, due to oxide of iron. It occurs in distinct crystals, sometimes minute and aggregated into masses, like the grains of sand in sandstone.

Quartz in some of its varieties occurs in almost every rock-stratum. It is an essential ingredient of granite, gneiss, mica-slate, and other allied rocks. The chalcedonic varieties occur principally in the vesicular cavities of basaltic and allied rocks. Flint occurs imbedded in chalk. Hornstone is sometimes imbedded in limestone. Jasper is also associated with limestone, and with basaltic rocks and porphyry.

Quartz-crystals sometimes occur of enormous size. A group in the Museum of the University at Naples weighs nearly half a ton. The British Museum also possesses some very large specimens.

Quartz is distinguished: 1. By its *hardness*, scratching glass with facility.—2. *Infusibility*, not fusing alone before the blowpipe.—3. *Insolubility*, not being attacked by water or acids.—4. *Uncleavability;* one variety indeed is tabular, but true cleavage is never observed.—5. The reaction with soda (p. 1). It is only pure quartz, however, that forms a clear glass.

QUARTZ-PORPHYRY. See Porphyry (iv. 691).—For analyses of several varieties of this rock, see Tribolet (Ann. Ch. Pharm. lxxxvii. 327; Jahresb. 1853, p. 868).

QUASSIA-CAMPHOR. A substance which separates from an aqueous infusion of quassia-wood, in white crystalline plates, lighter than water, and having the odour of the wood. (Bennerscheidt, Handw. d. Chem. vi. 741.)

QUASSIN. *Quassiin. Quassite.* $C^{10}H^{12}O^{3}$? (Winckler, Report, Pharm. liv. 85.—Wiggers, Ann. Ch. Pharm. xxi. 40.)—The bitter principle of quassia-wood (*Quassia amara*, L.). To extract it, the concentrated aqueous infusion of the wood, after being freed from pectin and other substances by treatment with slaked lime, is evaporated to dryness; the residue is digested in alcohol of 80 or 90 per cent.; the alcoholic solution is evaporated; the yellow, bitter, crystalline substance which remains is treated with a very small quantity of absolute alcohol; the resulting alcoholic solution is mixed with a large quantity of ether; and the filtered ethereal solution, after being concentrated by evaporation, is poured into a small quantity of water.

The liquid, if then left to itself, gradually deposits quassin in small white opaque prisms—very bitter, inodorous, and permanent in the air. It melts when heated, and forms, on cooling, a transparent, yellowish, very brittle mass. At a higher temperature it becomes more fluid, turns brown, carbonises, and then yields acid products free from ammonia; 100 pts. of water at 12° dissolve 0·45 pt. of quassin. Its solubility is increased by the presence of very soluble saline substances or organic acids. It contains, according to Wiggers, 65·7 per cent. carbon, and 6·9 hydrogen, agreeing very closely with the formula $C^{10}H^{12}O^{3}$. The aqueous solution gives a white precipitate with tannin, but is not precipitated by iodine, chlorine, mercuric chloride, iron-salts, or lead-salts. It dissolves without coloration in oil of vitriol, and in nitric acid of specific gravity 1·25; hot nitric acid converts it into oxalic acid.

QUASSITE. Syn. with Quassin.

QUEEN'S METAL. An alloy consisting of 9 pts. tin, 1 antimony, 1 lead, and 1 bismuth.

QUERÆSCITRIN. $C^{41}H^{46}O^{25}$. (Rochleder, Ann. Ch. Pharm. cxii. 112.)—A substance extracted by alcohol from the leaves of the chestnut (? horse-chestnut).* It forms fine yellow crystalline grains of the size of poppy-seeds, and is resolved by hydrochloric acid into quercetin and glucose:

$$C^{41}H^{46}O^{25} + 3H^{2}O = C^{23}H^{16}O^{10} + 3C^{6}H^{12}O^{6}.$$

QUERCETAMIDE. An ammoniacal solution of quercetin left to itself for two months, and then treated with hydrochloric acid, deposits unaltered quercetin; but on adding ammonia to the acid filtrate, quercetamide is obtained, as an orange-yellow precipitate, which alters very quickly on exposure to the air. At a temperature of 145° to 150°, this body is formed in twelve hours, but in a less pure state. It is amorphous, slightly soluble in water, more soluble in alcohol, ether, hydrochloric acid, and excess of ammonia. (Schützenberger and Paraf, Zeitschr. Ch. Pharm. 1862, p. 41.)

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* The substance is said by Rochleder to occur "in den Kastanienblättern;" but the name *queræscitrin*, which he gives to it, would seem to imply that it was obtained from the horse-chestnut (*Æsculus Hippocastanum*). See Quercetin.

QUERCETIC ACID. $C^{17}H^{12}O^8$, or $C^{21}H^{14}O^{10}$, or $C^{15}H^{10}O^7$? (Hlasiwetz, Ann. Ch. Pharm. cxii. 96.—Zwenger and Dronke, *ibid.* Suppl. i. 261; also cxxiii. 153.—Hlasiwetz and Pfaundler, J. pr. Chem. xciv. 65; Jahresb. 1864, p. 561.)—A compound formed, together with phloroglucin and other products, by the action of boiling potash on quercetin:

$$\underset{\text{Quercetin.}}{C^{23}H^{16}O^{10}} + H^2O = \underset{\text{Quercetic acid.}}{C^{17}H^{12}O^8} + \underset{\text{Phloroglucin.}}{C^6H^6O^3} \text{ (Hlasiwetz).}$$

$$\underset{\text{Quercetin.}}{3C^{13}H^{10}O^6} + H^2O = \underset{\text{Quercetic acid.}}{C^{21}H^{14}O^{10}} + \underset{\text{Phloroglucin.}}{3C^6H^6O^3} \text{ (Zwenger and Dronke).}$$

$$\underset{\text{Quercetin.}}{C^{27}H^{18}O^{12}} = \underset{\text{Quercetic acid.}}{C^{15}H^{10}O^7} + \underset{\text{Morin.*}}{C^{12}H^8O^5} \text{ (Hlasiwetz and Pfaundler).}$$

Preparation.—A hot very concentrated solution of 3 pts. potassium-hydrate is boiled down in a silver basin with 1 pt. quercetin, and the residue is heated, till a sample dissolved in water on a watch-glass no longer gives a flocculent precipitate (paradatiscetin) with hydrochloric acid, and the residue quickly turns dark-red at the edges; it is then immediately diluted with water, and neutralised with hydrochloric acid. After being left to cool and stand for a while, it is filtered from the separated flocks, which contain quercetin and paradatiscetin; the filtrate is evaporated to dryness; the residue exhausted with alcohol; the alcohol distilled off from the brown tincture; and the residue diluted with water. On adding neutral acetate of lead to this solution, quercetate of lead is precipitated (phloroglucin remaining in solution), which may be decomposed under water by sulphydric acid. After the sulphide of lead has been filtered off and washed with boiling water, the solutions are evaporated in a current of hydrogen, and the crystals, which separate after some days, are collected and decolorised by recrystallisation, with addition of animal charcoal (Hlasiwetz). Or the neutralised solution, mixed with one-fourth of its volume of alcohol, may be shaken up with ether, the ether evaporated, and the residue dissolved in water, and treated with acetate of lead as above. (Hlasiwetz and Pfaundler.)

Properties.—Quercetic acid crystallises in slender silky needles, which effloresce in a warm atmosphere, and give off 15·49 per cent. water between 120° and 131° ($C^{17}H^{12}O^8.HO^2$ requires 15·47 per cent.). The composition of the anhydrous acid, according to calculation and analysis, is as follows:

	Calculation.			*Mean of analyses.*
	Hlasiwetz. $C^{17}H^{12}O^8$	Zwenger and Dronke. $C^{21}H^{14}O^{10}$	Hlasiwetz and Pfaundler. $C^{15}H^{10}O^7$	Hlasiwetz.
Carbon . . .	59·30	59·15	59·60	59·44
Hydrogen . . .	3·48	3·28	3·31	3·73
Oxygen . . .	37·22	37·57	37·09	36·83
	100·00	100·00	100·00	100·00

The last formula agrees best with the analyses, but it does not afford so ready an explanation as the others of the simultaneous formation of phloroglucin from quercetin (p. 5).

Quercetic acid dissolves sparingly in cold, easily in boiling *water*; it is soluble also in *alcohol* and *ether*. The aqueous solution turns yellow when exposed to the air. A very dilute solution, when exposed to the air, acquires first a yellow, then a splendid carmine colour. The acid dissolves with red-brown colour in *oil of vitriol*, and is precipitated by water in red flocks, forming purple solutions with ammonia and potash (Hlasiwetz).—It is coloured black-blue by *ferric chloride*, or in very dilute solution, a splendid bright blue (Hlasiwetz). When dissolved in water together with *urea* it forms a compound, and with excess of *urea*, a product of decomposition (Pfaundler). By fusion with *potash*, it is converted into protocatechuic and quercimeric acids:

$$\underset{\text{Quercetic acid.}}{C^{15}H^{10}O^7} + H^2O + O = \underset{\text{Protocatechuic acid.}}{C^7H^6O^4} + \underset{\text{Quercimeric acid.}}{C^8H^6O^5}.$$

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* The morin is said to be further transformed into phloroglucin, with simultaneous formation of oxalic acid; but the mode of decomposition is not given.

Diaceto-quercetic acid. $C^{21}H^{16}O^{10} = C^{17}H^{10}(C^2H^3O)^2O^8$? (Pfaundler, Ann. Ch. Pharm. cxix. 813.)—Obtained by heating quercetic acid with chloride of acetyl to 100° in a sealed tube, expelling the excess of the chloride after the action is over, and drenching the residual glutinous mass with water. It then remains in resinous flocks, which may be purified by washing with water and crystallisation from alcohol. It is decomposed by heat, with formation of acetic acid. It reduces alkaline solutions of copper- and silver-salts; scarcely colours a solution of ferric chloride.

The above reaction also gives rise to the formation of a second product, probably *monoacetoquercetic acid*, which remains dissolved in alcohol, after the diaceto-compound has crystallised out, and is precipitated by water in white flocks; it colours ferric chloride deep green. (Pfaundler.)

QUERCETIN. *Meletin.*—A product of the decomposition of quercitrin and similar bodies, discovered in 1854 by Rigaud (Ann. Ch. Pharm. xc. 283), and further examined by Hlasiwetz (*ibid.* cxii. 96), who assigned to it the formula, $C^{23}H^{16}O^{10}$; by Zwenger and Dronke (*ibid.* Suppl. i. 21, and cxxiii. 153), who adopt the formula $C^{13}H^{10}O^6$, proposed by Wurtz (Ann. Ch. Phys. [3] xlii. 244); and lastly by Hlasiwetz and Pfaundler (J. pr. Chem. xciv. 65; Jahresb. 1864, p. 560), who regard it as $C^{27}H^{18}O^{12}$.

Quercetin is produced, together with sugar or a similar body, by boiling quercitrin (Rigaud), rutin (Rochleder and Hlasiwetz), or robinin (Zwenger and Dronke), with aqueous mineral acids, and separates during the boiling and on cooling, partly only after the liquid has been left at rest for some time. It is likewise obtained in the preparation of quercitrin by the method presently to be described (p. 6), and by the decomposition of several substances identical or isomeric with quercitrin, viz.—*α.* A yellow colouring-matter from ripe horse-chestnuts, likewise found in the full but not in the undeveloped leaves, and in the flowers (Rochleder).—*β.* A yellow dye from hops.—*γ.* A yellow dye from the berries of the sea-buckthorn or sallowthorn (*Hippophaë rhamnoïdes*).—*δ.* *Flavin*, a yellow-brown powder from North America (ii. 655).—*ε.* The green leaves and the flowers of plants contain either quercitrin or quercetin. (Filhol, J. Pharm. [3] xli. 151.)

Rhamnetin and thujetin are regarded by Hlasiwetz as identical with quercetin, which however is doubted by Bolley in the case of rhamnetin.

Quercetin forms either small, very slender, bright-yellow needles, which do not polarise light, or a lemon-yellow powder. It contains water of crystallisation, which, according to Hlasiwetz, is not completely expelled at 120°, or even between 200° and 220°. Hlasiwetz originally assigned to hydrated quercetin dried at various temperatures the formulæ $4C^{23}H^{16}O^{10}.H^2O$, $2C^{23}H^{16}O^{10}.H^2O$, and $C^{23}H^{16}O^{10}.H^2O$. According to the more recent experiments of Hlasiwetz and Pfaundler, anhydrous quercetin is $C^{27}H^{18}O^{12}$, and there are two hydrates containing $2C^{27}H^{18}O^{12}.H^2O$ and $C^{27}H^{18}O^{12}.H^2O$. [For analyses, see Gmelin's *Handbook*, xvi. 492, and the memoir of Hlasiwetz and Pfaundler above cited.]

Quercetin melts above 251° to a yellow liquid, without decomposition when quickly heated, and solidifies in the crystalline form on cooling. At a higher temperature, or when slowly heated even to 230°—250°, it sublimes with partial decomposition in yellow needles. It is inodorous, permanent in the air, and neutral.

Quercetin is nearly insoluble in cold, and but slightly soluble in boiling *water*, forming a yellow solution; easily in *alcohol* even when very dilute, much less freely in *ether*. It dissolves without decomposition in warm *acetic acid*, and in warm concentrated *hydrochloric acid*. From solution in alcoholic hydrochloric acid it separates on concentration in deep orange-yellow crystals.—Cold *nitric acid* dissolves it readily, and on heating the solution, oxalic acid is formed, together with a small quantity of picric acid.

Quercetin dissolves easily in alkaline liquids, forming golden-yellow solutions, from which it is precipitated in flocks by acids. It forms with *potash* the compound $C^{27}H^{18}O^{12}.K^2O$, or $C^{27}H^{16}K^2O^{12}.H^2O$, a corresponding compound with *soda*, and with *zinc-oxide* the compound $C^{27}H^{18}O^{12}.Zn''H^2O^2$. (Hlasiwetz and Pfaundler.)

The alcoholic solution of quercetin forms a brick-red precipitate with *neutral acetate of lead.*—*Ferrous chloride* colours the alcoholic solution dark-red, but scarcely affects the aqueous solution.—*Ferric chloride* colours the aqueous solution dark-green, even when very dilute, the colour changing to dark-red when heated. An alcoholic solution of quercetin mixed with alcoholic ferric chloride and evaporated, leaves a dark-green amorphous mass, nearly insoluble in water, but dissolving completely in alcohol and ether, the solutions having the colour of chlorophyll. (Pfaundler.)

Quercetin easily reduces *nitrate of silver* at ordinary temperatures, *chloride of gold* at the boiling heat, and *cupric oxide* in alkaline solution. When heated, or left for some time in contact with aqueous *ammonia*, it forms quercetamide. (Schützenberger and Paraf, p. 2.)

Quercetin heated with *potash* yields quercetic acid and other products, varying according to the duration of the action. When it is heated with 3 pts. potassium-hydrate till a sample dissolved in water exhibits a purple-red colouring on the edges, the product consists chiefly of quercetic acid, phloroglucin, and paradatiscetin,* $C^{15}H^{10}O^{6}$ (formerly called by Hlasiwetz *alpha-quercetin*, and regarded as $C^{29}H^{20}O^{12}$), which separates in yellow flocks on the addition of hydrochloric acid. If the action be further prolonged, protocatechuic and quercimeric acids are produced by the decomposition of the quercetic acid, also a body which has not been obtained in the free state, but remains in the mother-liquor from which the phloroglucin has been deposited, and is characterised by yielding a fine violet colour with carbonate of sodium and indigo-blue with strong sulphuric acid.

Hlasiwetz and Pfaundler regard quercetin as a compound of quercetic acid and morin:

$$\underset{\text{Quercetin.}}{C^{27}H^{18}O^{12}} = \underset{\text{Morin.}}{C^{12}H^{8}O^{5}} + \underset{\text{Quercetic acid.}}{C^{15}H^{10}O^{7}}$$

a view of its composition which explains the formation of quercetic, quercimeric, and protocatechuic acids, but not that of paradatiscetin. The quercimeric and protocatechuic acids are formed as shown by the equation already given (p. 4). The phloroglucin appears to be formed from paradatiscetin, thus:

$$2C^{15}H^{10}O^{6} + 5H^{2}O + O^{4} = 5C^{6}H^{6}O^{3}.$$

The quantity of phloroglucin produced is greater as the action is more prolonged. [The mode of formation of quercetic acid and phloroglucin according to the older formulæ of quercetin has been already given, p. 3.]

When a solution of quercetin in dilute soda-ley is treated with *sodium-amalgam* (containing 3 or 4 per cent. sodium) till the liquid has acquired a light brownish-yellow colour, then neutralised with hydrochloric acid, and shaken up with ether, the ether extracts phloroglucin, together with two other bodies which may be separated by precipitation with acetate of lead. On decomposing the precipitate with sulphydric acid, and evaporating the filtrate in a vacuum, a crystalline powder is first deposited, consisting of a body, A, having the composition $C^{13}H^{12}O^{5}$, while another body B, consisting of $C^{7}H^{8}O^{3}$, separates in granular crystals from the mother-liquid after longer standing and repeated evaporation.

The less soluble body A is a weak acid, which crystallises from hot water in slender prisms, and dissolves easily in alcohol and ether; its alcoholic solution is coloured dark-violet by ferric chloride, and violet changing to brown-yellow by potash. By renewed treatment with sodium-amalgam it is converted into phloroglucin; by fusion with potash, into phloroglucin and protocatechuic acid:

$$C^{13}H^{12}O^{5} + O^{2} = C^{6}H^{6}O^{3} + C^{7}H^{6}O^{4}.$$

The other body B is also a weak acid: it melts at 130°; its aqueous solution is coloured dark yellow-red by a drop of caustic potash, green by ferric chloride, and then purple-violet on addition of sodic carbonate. It reduces silver-solution and alkaline cupric solutions, and is converted by fusion with potash into protocatechuic acid:

$$C^{7}H^{8}O^{3} + H^{2}O = C^{7}H^{6}O^{4} + 2H^{2}.$$

An alcoholic solution of quercetin acidulated with hydrochloric acid is converted by sodium-amalgam into a red body (Stein's *paracarthamin*, iv. 341), which is easily reconverted into quercetin. (Hlasiwetz and Pfaundler.)

QUERCIMERIC ACID. $C^{8}H^{10}O^{5}$.—Produced by the action of melting potash on quercetic acid, or by its prolonged action on quercetin. When quercetin is fused with hydrate of potassium till the mass no longer froths up in large bubbles, and a sample of it dissolves, no longer with golden-yellow, but with tawny-yellow colour, changing to red more quickly on exposure to the air, quercimeric acid is sometimes found in the solution, instead of, or together with, quercetic acid, and separates from the mother-liquor in granular crystals, which may be purified by repeated fractional crystallisation and decolorisation with animal charcoal, or by decomposition of the lead-precipitate with sulphydric acid.

Quercimeric acid in the crystalline state contains $C^{8}H^{6}O^{5}.H^{2}O$. It is colourless, has an acid reaction and astringent taste, dissolves readily in water, alcohol, and ether, and separates therefrom, in granular or small prismatic crystals. The aqueous solution immediately becomes purple-red on addition of a trace of alkali, dark-blue with ferric chloride. Like quercetic acid, it reduces nitrate of silver and alkaline cupric solutions, and is precipitated by acetate of lead. When fused with potash, it yields protocatechuic acid:

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* To obtain this substance pure, it is dissolved in alcohol; the solution is mixed with acetate of lead, which throws down quercetin; the liquid freed from lead by sulphuric acid, and concentrated to two-thirds, is mixed with water; and the flocks thereby separated are crystallised from very weak spirit. Paradatiscetin is thus obtained in yellowish needles. It is probably isomeric with datiscetin (ii. 306) and luteolin (iii. 736); dissolves easily and with acid reaction in dilute alcohol, less easily in alcohol, and is nearly insoluble in water. The alcoholic solution is coloured violet by ferric chloride, yellow by potash, turning green on exposure to the air, red or red-brown by aqueous bromine or chlorine. It reduces nitrate of silver and alkaline cupric solutions when heated with them. When boiled with alkaline earths, it yields hydrated salts crystallising in long needles. By fusion with hydrate of potassium it yields phloroglucin, but no quercetic or protocatechuic acid. (Hlasiwetz and Pfaundler.)

$$C^8H^6O^5 + O = C^7H^6O^4 + CO^2.$$

QUERCITANNIC ACID. An acid of unknown composition, extracted from oak-bark, and exhibiting with ferric salts the same reactions as gallotannic acid. It differs however from the latter in not being convertible into gallic acid, and not yielding pyrogallic acid by dry distillation. It is precipitated by sulphuric acid in red flocks. (Stenhouse, Ann. Ch. Pharm. xlv. 16.)

According to Rochleder (*ibid.* lxiii. 202), the tannic acid of black tea is the same as that of oak-bark.

QUERCITE. $C^6H^{12}O^5$. *Quercin. Sugar of Acorns.* (Braconnot, Ann. Ch. Phys. [3] xxvii. 392.—Dessaignes, Ann. Ch. Pharm. lxxxi. 103 and 251.)—A saccharine substance contained in acorns. To prepare it, the aqueous extract of bruised acorns is freed from dissolved tannic acid by heating it with lime; the filtrate is left to ferment with yeast, to remove fermentable sugar; the filtered liquid is evaporated to a syrup; and the crystals which separate after a while, are washed with alcohol, and recrystallised from water or weak spirit.

Quercite forms hard monoclinic crystals, grating between the teeth. It is permanent in the air, and does not alter even at 215°, but melts at 235°, with partial sublimation and slight carbonisation. It dissolves in 8 to 10 parts of water, forming a solution which takes up a small quantity of lime; also in hot dilute alcohol.

Quercite triturated with strong *sulphuric acid*, forms a conjugated acid, the calcium-salt of which does not crystallise. By hot *nitric acid* it is converted into oxalic, not into mucic acid. A mixture of *nitric* and *sulphuric acids* converts it into nitroquercite, which is a white amorphous resin, insoluble in water, soluble in hot alcohol, reduced to quercite when its alcoholic solution is treated with sulphydric acid.

With *baryta*, quercite forms a compound containing $C^{12}H^{24}O^{10}.Ba''O.2H^2O$. It forms a white precipitate with a warm solution of *basic lead-acetate* mixed with ammonia.

Benzoquercite, $C^{20}H^{20}O^7 = C^6H^{10}O^5.(C^7H^5O)^2$.—A solid neutral compound produced by heating quercite with benzoic acid to 200° in sealed tubes. It is insoluble in water, soluble in ether and in alcohol. When dissolved in absolute alcohol and treated with hydrochloric acid gas, it is resolved into quercite and ethylic benzoate. (Berthelot, Compt. rend. xliv. 452.)

Stearoquercite, $C^{42}H^{80}O^7 = C^6H^{10}O^5.(C^{18}H^{35}O)^2$, is a white solid mass, which reacts like the preceding, and is obtained in a similar manner. (Berthelot.)

Quercitartaric acid, $C^{22}H^{32}O^{27} = C^6H^{12}O^5 + 4C^4H^6O^6 - 2H^2O$, is obtained like dulcitartaric acid (ii. 348) from quercite and tartaric acid. Its *calcium-salt*, $C^{22}H^{26}Ca^3O^{27}.2H^7O$, gives off 16·1 per cent. water at 110°. (Berthelot, Ann. Ch. Phys. [3] liv. 82.)

QUERCITRIN. *Quercitric Acid. Quercimelin.*—A neutral substance occurring in quercitron-bark, the bark of *Quercus tinctoria.*

Preparation.—1. The bark is boiled with water, the decoction is left to cool, and the impure quercitrin which separates is collected, then rubbed to a pulp with alcohol of 35° B., heated over the water-bath, collected on linen, and pressed, whereby the principal impurities are removed. The residue is dissolved in a larger quantity of boiling alcohol, the solution is filtered hot, and water is added to it till it becomes turbid, so that the greater part of the quercitrin separates before the liquid is quite cold. It is then collected, pressed, and purified by a repetition of the same treatment (Rochleder, J. pr. Chem. lxxvii. 34).[*]—2. The pulverised bark is exhausted with six parts alcohol of specific gravity 0·84 in a percolator, till the liquid is of a bright wine-yellow colour. The tincture is freed from tannic acid by precipitation with washed ox-bladder or isinglass-solution, and filtered; and after adding water, the alcohol is distilled off, when a quantity of brown resinous drops first separates, and afterwards quercitrin crystallises out. The crystals must be collected before remaining too long in the mother-liquor, then washed with cold water, and dissolved in absolute alcohol; and the filtrate, after addition of water, evaporated till it crystallises (Bolley, Ann. Ch. Pharm. xxxvii. 101; lxii. 136.—Rigaud, *ibid.* xc. 283).—3. The bark, in small pieces, is exhausted with boiling alcohol; the alcohol is distilled off; and the residue, while still warm, is mixed with a little acetic acid, and then with neutral acetate of lead; the filtrate, freed from lead by sulphydric acid, is evaporated; and the quercitrin which crystallises is purified by repeated crystallisation from alcohol (**Zwenger** and **Dronke**, Ann. Ch. Pharm. Suppl. i. 266).—**Stein** (J. pr. Chem. lxxxv. 351) apprehends, in this process, a decomposition of the quercitrin by the free acetic acid.

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[*] The quercitrin remaining in the bark is obtained as quercetin by decomposing a second decoction with hydrochloric acid in the cold, then filtering, and heating to the boiling-point, the quercetin then separating. It is to be filtered whilst hot, as afterwards only a little impure quercetin is deposited from the solution. (Rochleder.)

Properties.—Hydrated quercitrin forms microscopic, partly rectangular, partly rhombic tablets having their obtuse lateral edges truncated; pale-yellow when pulverised. It is neutral, inodorous, tasteless in the solid state, bitter in solution, permanent in the air.

Air-dried quercitrin heated to 100° gives off, on the average, 5·74 per cent. water, and when heated to 165° for some time, a further quantity, amounting altogether to 11·81 per cent. of the air-dried substance. After dehydration, the quercitrin melts at 160° to a dark-yellow resin, which solidifies to an amorphous mass on cooling. (**Zwenger** and **Dronke**.)

Hlasiwetz and **Pfaundler** (Jahresb. 1864, p. 564) give for anhydrous quercitrin the formula $C^{33}H^{30}O^{17}$, and state that it forms three hydrates—$C^{33}H^{30}O^{17}.H^2O$, $C^{33}H^{30}O^{17}.2H^2O$, and $C^{33}H^{30}O^{17}.3H^2O$. Several other formulæ have been proposed for quercitrin. Hlasiwetz at different times assigned to it the formulæ $C^{29}H^{30}O^{17}$ and $C^{35}H^{36}O^{20}$, while Zwenger and Dronke regard it as $C^{19}H^{18}O^{10}$. It is by no means certain that the so-called quercitrins examined by these several chemists are identical with one another (p. 4). [For analyses and calculations, see Gmelin's *Handbook*, xvi. 497.]

Quercitrin is slightly soluble in cold, somewhat more soluble in boiling *water*; much more soluble in *alcohol*, slightly in *ether*. It dissolves also in warm *acetic acid*, in dilute aqueous *ammonia*, and in caustic *soda*; the ammoniacal solution gradually deepens in colour on exposure to the air.

Quercitrin is almost wholly precipitated from its solution by *neutral* or *basic acetate of lead*, the precipitate being readily soluble in acetic acid. Aqueous or alcoholic quercitrin is coloured dark-green by *ferric chloride*, even when diluted to 4,000 or 5,000 times its bulk (**Rigaud**). It is not coloured at first by *ferrous chloride*, but the solution turns greenish on exposure to the air. (**Zwenger** and **Dronke**.)

Decompositions.—1. Quercitrin yields, by dry distillation, empyreumatic products, together with yellow crystals of quercetin, and leaves a light difficultly combustible charcoal.—2. Solutions of quercitrin acquire a brown-red colour by exposure to the air (**Bolley**). Concentrated *nitric acid* produces a violent evolution of nitric oxide and carbonic anhydride, and forms a clear red-brown solution containing oxalic acid (**Rigaud**). Besides a large quantity of oxalic acid, there is produced a trace of picric acid (**Zwenger** and **Dronke**); none according to **Stenhouse** (Ann. Ch. Pharm. xcviii. 179). Dilute nitric acid, when warmed with quercitrin, produces at first the same splitting-up as other acids, afterwards more complete decomposition (**Rigaud**).—4. Quercitrin, heated with *oxide of manganese* and sulphuric acid (**Bolley**), with *chromate of potassium* and sulphuric acid (**Rigaud**), yields formic acid.—5. The dark-brown precipitate produced by *nitrate of silver* in solutions of quercitrin is quickly reduced to the metallic state (**Bolley**). Quercitrin reduces *nitrate of silver* and *trichloride of gold* quickly in the cold, *cuprate of potassium* only after continued boiling or long standing (**Zwenger** and **Dronke**).—6. *Oil of vitriol* forms with it a solution which soon becomes dark and black (**Rigaud**).—7. Quercitrin is decomposed, by boiling with dilute *mineral acids*, into quercetin, which separates, and a saccharine substance, also according to Rigaud by boiling with alum, but not by prolonged heating with acetic acid. The decomposition is not effected by emulsin (**Zwenger** and **Dronke**). According to Hlasiwetz and Pfaundler, the sugar produced is **isodulcite**, $C^6H^{14}O^6$,

$$\underset{\text{Quercitrin.}}{C^{33}H^{30}O^{17}} + H^2O = \underset{\text{Quercetin.}}{C^{27}H^{18}O^{12}} + \underset{\text{Isodulcite.}}{C^6H^{14}O^6}.$$

100 pts. of anhydrous quercetin were found to yield 25·5 pts. isodulcite; calculation requires 26·4 pts. Hlasiwetz formerly found 27·87 per cent. sugar, which he regarded as isomeric with glucose, representing its formation by the equation,

$$\underset{\text{Quercitrin.}}{C^{29}H^{30}O^{17}} = \underset{\text{Quercetin.}}{C^{23}H^{16}O^{10}} + \underset{\text{Sugar.}}{C^6H^{12}O^6} + H^2O,$$

which requires 27·4 per cent. Rigaud, on the other hand, found that 100 pts. of quercitrin yielded on the average 44·35 pts. sugar and 61·44 quercetin, and Stein obtained 62·9 pts. quercetin. These numbers agree approximately with the equation given by Zwenger and Dronke:

$$\underset{\text{Quercitrin.}}{C^{19}H^{18}O^{10}} + 2H^2O = \underset{\text{Quercetin.}}{C^{13}H^{10}O^6} + \underset{\text{Sugar.}}{C^6H^{12}O^6},$$

which requires 60·50 per cent. quercetin and 41·57 sugar. The great divergences in these results seem to indicate that substances differing from one another in constitution have been confounded together under the name of quercitrin.

QUERCITRON. A yellow dye-stuff consisting of the shavings and powder of the bark and alburnum of *Quercus tinctoria*, *Q. nigra*, or *Q. citrina*, a kind of oak indigenous in North America, especially in Carolina, Georgia, and Pennsylvania. It is used in America for tanning, in Europe for dyeing only. For the latter purpose, the aqueous decoction (which contains quercitrin) mordanted with alum or stannic chloride is employed. According to Leesching (Rep. of Patent Inventions, Jan. 1856, p. 55), a product of greater colouring power may be obtained by boiling the bark with dilute sulphuric acid or hydrochloric acid. This result is probably due to the conversion of the quercitrin into quercetin, which, according to Rigaud, produces much purer and brighter colours on tissues than quercitrin.

QUERCUS. *Oak.*—The wood of *Quercus sessiliflora*[*] has a specific gravity of 0·65, and in the air-dried state contains 48·8 per cent. carbon, 6·1 hydrogen, and 45·1 oxygen (Schadler and Petersen, Ann. Chem. Pharm. xvii. 139). Vogel (N. Jahresb. Pharm. vii. 367) found 49·5 C to 5·3 H, 43·7 O, and 1·5 ash; in the mould of oak-wood 52·5 C to 5·0 H, 40·6 O, and 1·9 ash. Sprengel (J. Techn. Chem. xiii. 383) found in the air-dried wood only 0·20 per cent. ash.

The leaves of the oak contain, according to Sprengel, 48 pts. water and 52 pts. dry substance, 25 pts. of which are soluble in water, and 57 pts. in dilute potash-ley. According to Boussingault (Ann. Ch. Phys. [2] lxvii. 408), 100 pts. of the dried leaves contain 2·1 per cent. nitrogen, and according to Sprengel, 100 pts. of the air-dried leaves yield 5·06 per cent. ash.

Oak-bark contains, besides quercitannic acid (p. 6), a small quantity of gallic acid, red tannin-deposit (oak-red), wax, pectin, and other vegetable constituents; it also yields 2 per cent. ash, consisting of lime, magnesia, oxides of iron and manganese, phosphoric, silicic, and carbonic acid. The proportion of soluble constituents in general and of tannin in particular, is less in old than in young bark, less also in the outer than in the inner bark. Davy (Gehl. N. Chem. J. iv. 343) found in 100 pts. of oak-bark,

	Extractive matter.	Tannin.
Inner white bark of old oaks	22·5	15·0
Inner white bark of young oaks	23·5	16·0
Entire bark in spring	12·7	6·0
Entire bark in autumn	—	4·4
Bark of oak underwood	—	6·6
Middle coloured bark	9·0	4·0

Fehling (Wurtemb. Gewerbebl. 1856, p. 77) found in old oak-bark about 9 per cent., in bark of better quality from 13 to 16 per cent., and in the best inner bark 19 to 21 per cent. tannin. Müller (Arch. Pharm. xxxviii. 266) obtained from the bark of stems two or three years old, about 11 per cent., and from that of older stems 5 per cent. tannin.

The barks of *Quercus sessiliflora*, *Q. pedunculata*, and *Q. Ilex* are extensively used in tannin. Oak-bark has also been used for the preparation of inks, and in medicine for its styptic and astringent qualities.

Acorns, *Glandus quercus*, the fruit of the oak, have been examined by several chemists. The shell or cup constitutes about one-fourth of the entire fruit. Shelled acorns contain, according to Brande, 20·3 per cent. starch, 2·9 tannin, 51·7 extractive matter and water, 7·1 wood-fibre, and 18·0 per cent. gluten. The results of analyses by other chemists are as follows:

Composition of shelled acorns.

	Löwig.	Braconnot.	v. Bibra.
Starch	38·0	37·0	34·9
Uncrystallisable sugar	—	7·0	8·1
Gum and extractive matter	6·4	5·0	—
Nitrogenous substances	—	15·0	7·3
Tannic acid	9·0	—	7·0
Fixed oil	4·3	3·3	3·8
Woody fibre	1·9	31·9	—
Water	—	31·8	
Vegetable mucilage, gum, woody fibre, &c.	—	—	44·0

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[*] This is the common oak in Germany and the South of Europe, and is known as *Quercus Robur*. In England the latter term is applied to *Q. pedunculata*, which is the most common at the present day; but in former times, the sessile-fruited oak, which is a larger and finer tree and produces more durable *timber* than the pedunculated species, was the most abundant (see *Penny Cyclopædia*, article QUERCUS).

Braconnot also found citric acid and quercite in acorns. According to v. Bibra, they also contain a small quantity of volatile oil.

An infusion of roasted acorns (*acorn coffee*) is sometimes recommended as a tonic and astringent. The roasting converts part of the starch into dextrin, and forms bitter matter and empyreumatic oil.

The ash of acorns has been analysed:—*a.* By Graham, Stenhouse, and Campbell (Chem. Soc. Q. J. ix. 33); *b.* by Kleinschmidt (Ann. Ch. Pharm. l. 117), with the following results:—

	K^2O.	Na^2O.	CaO.	MgO.	Fe^2O^3.	P^2O^5.	SiO^2.	SO^3.	Cl.	CO^2.	
a.	54·9	0·6	6·1	4·3	0·5	11·1	1·0	4·8	2·5	13·7	= 99·5
b.	64·6	0·5	6·9	5·6	1·4	17 0	1·0	2·7	0·6	—	= 100·3

The cups of the acorns of *Quercus Ægilops* are imported from Smyrna, Cyprus, and other places in the Levant as *Valoniæ;* they are very rich in tannin, and are therefore used in place of gall-nuts; they likewise contain gallic acid. The tannin contained in them differs, however, from gallo-tannic acid, in not yielding pyrogallic acid by dry distillation. (Stenhouse.)

The cups of various kinds of oak, when distorted by the punctures of the gall-wasp, form the so-called oak-apples. These are also used in tanning, but they contain only a small proportion of tannic acid. The true gall-nuts or nut-galls are excresences produced on the leaves and leafstalks of the dyer's oak (*Quercus infectoria*), by the punctures of the same insect (ii. 762).

QUICKSILVER. Syn. with MERCURY.

QUILLAYA. The bark of *Quillaya saponaria*, a tree growing in Mexico, yields a soapy infusion, which is used for washing. It contains a considerable quantity of saponin; also deposits of crystalline oxalate and tartrate of calcium, formerly mistaken for sulphate. (Flückiger, Jahresb. 1862, p. 524; 1863, p. 610.)

QUILLAYIN. A name applied to saponin from quillaya-bark, before its identity with saponin from other sources was recognised.

QUINANILIDE, or *Phenyl-quinamide.* $C^{13}H^{17}NO^5 = N.C^7H^{11}O^5.C^6H^5.H.$ (O. Hesse, Ann. Ch. Pharm. cx. 335.)—This compound is produced by heating quinic acid with excess of aniline to 180°, freeing the product from unaltered aniline by means of ether, and dissolving the residue in ether-alcohol. The solution on cooling deposits quinanilide in small white silky needles, containing 1 at. water, which they give off at 90°. It melts at 174° (corrected), and decomposes without subliming when heated above 240°. It dissolves easily in water and in alcohol, sparingly in ether.

QUINCE. *Cydonia vulgaris.*—The juice of quinces contains malic acid. Lancaster (Am. J. Pharm. xxxi. 198) obtained 1·6 grm. crystallised malate of lead from the acid contained in 453 grms. of the fruit. The seeds contain a large quantity of mucilage (ii. 953).

QUINCITE. A hydrated silicate of magnesium, occurring near the village of Quincey in France, in light carmine-red particles disseminated through a limestone deposit. Contains, according to Berthier, 64 per cent. silica, 19 magnesia, 8 ferrous oxide, and 17 water (= 98). Strong concentrated acids dissolve out the magnesia and iron, leaving gelatinous silica. (Dana, ii. 281.)

QUINETIN. The name given by Marchand (J. Pharm. xiv. 247) to a product which he obtained by oxidising quinine with peroxide of lead and sulphuric acid. It was not, however, a definite compound, as it was separable by water into a red bitter substance, soluble therein, and another substance insoluble in water but crystallisable from alcohol.

QUINHYDRONE. Green Hydroquinone (iii. 213).

QUINIC ACID. $C^7H^{12}O^6$. *Kinic acid. Chinasäure. Acide quinique.* (Hofmann, Crell. Ann. ii. 314.—Vauquelin, Ann. Chim. lix. 162.—Pelletier and Caventou, Ann. Ch. Phys. [2] xv. 340.—Liebig, Pogg. Ann. xxi. 1; xxix. 70.—Baup, Ann. Ch. Phys. [2] li. 5.—Woskresensky, Ann. Ch. Pharm. xxiv. 257.—Hesse, Ann. Ch. Pharm. cx. 194, 333; cxii. 52; cxiv. 292; *Untersuchungen über die Chinongruppe*, Göttingen, 1860.—Clemm, Ann. Ch. Pharm. cx. 345.—Zwenger and Siebert, *ibid.* cxv. 108; Suppl. i. 77.—Zwenger and Himmelmann, *ibid.* cxxix. 203.—Gm. xvi. 222).

This acid was first isolated in 1785 by Hofmann, an apothecary of Leer, from the calcium-salt of cinchona-barks, already known by the researches of Hermbstädt, Deschamp, and others; afterwards, in 1806, by Vauquelin.

Occurrence.—In the true cinchona-barks, in the bilberry plant (*Vaccinium Myrtillus*), and in coffee-beans; also in the leaves of the coffee-plant, and of the common holly (*Ilex Aquifolium*), of *Ilex paraguayensis*, privet (*Ligustrum vulgare*), ivy (*Hedera Helix*), the common oak (*Quercus Robur*), the evergreen oak (*Q. Ilex*), the common elm (*Ulmus campestris*), the ash (*Fraxinus excelsior*), and *Cyclopia latifolia*, inasmuch as Stenhouse (Phil. Mag. [4] vii. 21) found that all these leaves, as well as coffee-beans, when distilled with sulphuric acid and manganic peroxide, yield quinone, which is a product of the decomposition of quinic acid. The ericaceous plants, *Calluna vulgaris*, *Pyrola umbellata*, *Rhododendron ferrugineum*, and *Arbutus Uva Ursi*, yield by dry distillation hydroquinone,* also derived from quinic acid, or, in the case of the arbutus, probably from arbutin.

Preparation of the calcium-salt.—a. From Cinchona-bark: 1. The liquid obtained by precipitating the sulphuric acid extract with milk of lime in the preparation of quinine (p. 16), is evaporated to a syrup, decanted from sulphate of calcium, and evaporated over the water-bath to a soft extract; this is boiled two or three times with alcohol; and the residue is dissolved in a small quantity of water. The solution, after standing for some days, solidifies to a crystalline mass, which is strongly pressed and purified by recrystallisation. The mother-liquor yields a further quantity of the salt (Henry and Plisson).—2. A decoction of cinchona-bark, in water containing sulphuric acid, is filtered whilst hot, and to the filtrate freshly precipitated oxide of lead is gradually added, until the liquid becomes neutral, and exhibits no longer a red but a pale-yellow colour. (If too little oxide be added, colouring-matter remains in solution; if too much, basic quinate of lead is thrown down). The filtrate is freed from lead by sulphydric acid and filtered; milk of lime is then added, to precipitate the quinine and cinchonine; and the filtered liquid is evaporated to a syrup, which yields, on cooling, a crystalline mass of calcic quinate (Henry and Plisson).—The deposit frequently found in extract of cinchona is impure quinate of calcium; it may be obtained in crystals by precipitating an aqueous solution with neutral acetate of lead, removing the excess of lead by sulphydric acid, and evaporating. (Oenicke, Pharm. Centr. 1838, p. 158.)

β. From the Bilberry plant.—The fresh plant, collected in May, is boiled in water with addition of lime; the decoction is evaporated, and the quinate of calcium thrown down by alcohol. The glutinous precipitate, dissolved in water containing acetic acid, is freed from colouring-matter by addition of neutral acetate of lead, then filtered; and the filtrate (freed from lead) is evaporated to a syrup, from which the quinate of calcium crystallises after some days. (Zwenger.)

γ. From Coffee-beans.—The thoroughly-dried (or roasted) and coarsely-powdered beans are boiled repeatedly in water; the decoction, after being mixed with milk of lime, is concentrated, first over an open fire, and later, after filtration, on a water-bath, to a syrup; twice its volume of alcohol is then added; and the precipitate thereby formed is separated, after 24 hours, from the solution, which contains caffeine. The precipitate is washed with alcohol, pressed, and dissolved in hot water. The filtered solution is slightly acidified with acetic acid, and precipitated with neutral acetate of lead, whereby tannate of lead and other substances are thrown down; and after separating these by filtration, the quinic acid is precipitated by basic acetate of lead. The lead-salt thus obtained, after being washed and decomposed under water with sulphydric acid, yields aqueous quinic acid, which is converted into the calcium-salt by neutralisation with carbonate of calcium. (Zwenger and Siebert.)

The quinate of calcium is purified by repeated crystallisation, or by precipitating it with alcohol of sp. gr. 0·849, and dissolving in alcohol of sp. gr. 0·948.

Separation of the acid from the calcium-salt.—1. A solution of the calcium-salt in water is decomposed by an exactly equivalent quantity of oxalic acid, filtered from the oxalate of calcium, and evaporated to crystallisation (Vauquelin). Hesse employs a slight excess of oxalic acid, which he removes from the filtrate by means of neutral acetate of lead; the excess of lead is then removed by sulphydric acid.—2. An aqueous solution of the salt is precipitated by basic acetate of lead; the washed precipitate, suspended in water, is then decomposed by sulphydric acid; and the solution is filtered and evaporated (Berzelius).—3. The calcium-salt is decomposed by an aqueous or alcoholic solution of sulphuric acid.

Properties—Quinic acid crystallises in monoclinic prisms, $\infty P . oP$, with $nP\infty$ and $[nP\infty]$ subordinate; sometimes oP predominates so far as to give the crystals a tabular form. Angle $\infty P : \infty P = 146° 48'$; $\propto P : oP = 125° 45'$. Specific gravity $= 1·637$ at 8·5°. The acid does not lose weight at 100°, but melts, with loss of water, at 161·6° corrected (Hesse; Zwenger and Siebert); at 155° (Woskresensky), and solidifies on cooling to a hard amorphous mass. It exerts a left-handed action on polarised light, the molecular rotatory power being greater in a solution prepared with cold than in one prepared with hot water, least of all in a solution of the fused acid. (Hesse.)

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* The hydroquinone thus produced was regarded by Uloth, who first obtained it from ericaceous plants, as a distinct substance, and called *ericinone*. Hesse, however, suggested its identity with hydroquinone, and the correctness of this view has been demonstrated by Zwenger and Himmelmann.

Quinic acid dissolves slowly in 2½ pts. of cold *water*, and in a much smaller quantity of boiling water. The solution, if quite pure, may be evaporated without turning yellow. The acid is very slightly soluble in *alcohol* of 94 per cent., but dissolves easily in alcohol of ordinary strength; it is nearly insoluble in cold *ether*.

Decompositions.—1. Quinic acid heated to 200°—225° gives off water, and is converted into quinide, $C^7H^{10}O^5 = C^7H^{12}O^6 - H^2O$. Other products are, however, formed at the same time: for the calculated loss of water, according to the preceding equation, is 9·95 per cent, whereas, according to Hesse, 10 per cent. are given off at 165°, and more than 13 per cent. at 220°. Quinic acid which has been heated above 200° contains small quantities of carbohydroquinonic acid (iii. 214), recognisable by its reaction with ferric chloride (Hesse).—2. The acid, when quickly heated in contact with the air, burns with a yellow flame, emitting an odour like that of burnt tartar.

3. Quinic acid subjected to dry distillation in a retort, melts, boils, and at about 280° turns brown, giving off water and a gas which burns with a pale-blue flame. At a higher temperature, it yields a sublimate of yellowish prisms, which melt and condense to an oily distillate containing hydroquinone (iii. 213), benzoic acid, phenol, benzene, and pyrocatechin.* The formation of hydroquinone is represented by the equa-acid:

$$C^7H^{12}O^6 = C^6H^6O^2 + CO + 3H^2O.$$

4. Quinic acid dissolves in strong *sulphuric acid* at a moderate heat, with evolution of carbonic oxide and formation of disulpho-hydroquinonic acid (iii. 217):

$$C^7H^{12}O^6 + 2SO^3 = C^6H^6S^2O^8 + CO + 3H^2O.$$

Sulphuric anhydride and fuming sulphuric acid also produce disulpho-hydroquinonic acid, but carbonise a large quantity of the quinic acid (Hesse).—5. A solution of quinic acid in aqueous *phosphoric acid* gives off a large quantity of gas when concentrated, and forms phospho-hydroquinonic acid (iii. 217):

$$C^7H^{12}O^6 + H^3PO^4 = C^7H^7PO^5 + CO + 4H^2O \text{ (Hesse).}$$

6. *Nitric acid* converts quinic acid into oxalic acid, another acid which has not been examined being also formed at the beginning of the action.—7. The aqueous acid treated with *peroxide of lead* gives off carbonic anhydride and yields hydroquinone (Hesse):

$$C^7H^{12}O^6 + PbO^2 = C^6H^6O^2 + CO^2 + 3H^2O + PbO.$$

8. Quinic acid or its salts distilled with *sulphuric acid* and *peroxide of manganese*, yields a yellow crystalline sublimate of quinone:

$$C^7H^{12}O^6 + O^2 = C^6H^4O^2 + CO^2 + 4H^2O.$$

This reaction is very delicate, and will indicate the presence of quinic acid in a few grammes of cinchona-bark. For this purpose the bark is boiled with milk of lime, and the alkaline filtrate concentrated by evaporation is treated in a small capsule with sulphuric acid and oxide of manganese: the presence of quinic acid is then immediately indicated by the pungent odour of quinone (p. 27), (Stenhouse, Ann. Ch. Pharm. liv. 100).—9. The acid distilled with *peroxide of manganese*, *sulphuric acid*, and *common salt*, yields a distillate containing mono-, di-, tri- and tetrachloroquinone together with pentachloracetone. The same products, together with lower chlorinated acetones, are obtained by boiling quinic acid with hydrochloric acid and chlorate of potassium (Städeler, Ann. Ch. Pharm. lxix. 300; cxi. 293); also carbohydroquinonic acid. (Hesse.)

10. *Bromine* dropped into aqueous quinic acid converts it into carbohydroquinonic acid.

11. Quinic acid heated for several hours to 115°—120° with saturated aqueous *hydriodic acid*, is converted into benzoic acid. The same product is formed when a syrupy solution of quinic acid is distilled with 4 at. diniodide of phosphorus. When quinic acid is heated to 140° with hydriodic acid and phosphorus (the addition of which prevents the action of free iodine), an acid is produced containing 6 at. hydrogen more than benzoic acid. The reduction appears, therefore, to take place as follows:—

$$\underset{\text{Quinic acid.}}{C^7H^{12}O^6} + 8HI = C^7H^{12}O^2 + 4H^2O + 4I^2;$$

and

$$C^7H^{12}O^2 + 4I^2 = \underset{\text{Benzoic acid.}}{C^7H^6O^2} + 6HI + I^2.$$

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* Wöhler (Ann. Ch. Pharm. xlv. 354) found also salicylous acid; but according to Zwenger and Himmelmann, this body does not occur among the products of distillation of quinic acid.

Quinic acid in the form of calcium-salt is converted in the animal organism into hippuric acid. (Lautemann, Ann. Ch. Pharm. cxxv. 9.)

12. Quinic acid heated with *aniline* is converted into quinanilide. (Hesse, p. 9.)

Quinates. Quinic acid decomposes carbonates. It is monobasic, the general formula of its salts being $C^7H^{11}MO^6$. No acid or double quinates are known, but basic quinates of barium, lead, iron, and copper have been obtained. The quinates are for the most part crystallisable, and have a neutral reaction; with the exception of the basic lead-salt they are soluble in water, but insoluble in alcohol stronger than 32° Bm., and are separated from their solution by strong alcohol in the form of glutinous precipitates. Most of them retain their water of crystallisation at 100°. By dry distillation they yield formic acid and a sublimate of quinone (Woskresensky). Quinic acid acts like tartaric acid in preventing the precipitation of metallic oxides by alkalis. (Hesse.)

Quinate of Ammonium is deliquescent, and gives off part of its ammonia on evaporation.—The *potassium-salt* is bitter and deliquescent.—The *sodium-salt*, $C^7H^{11}NaO^6.5H^2O$, crystallises in six-sided prisms containing 14·5 per cent. water of crystallisation. It dissolves in half its weight of water at 15°.

Quinate of Barium, $C^{14}H^{22}Ba''O^{12}.6H^2O$, obtained by saturating the acid with carbonate of barium, crystallises in dodecahedrons formed by the junction of two acute six-sided pyramids. It contains 17·4 per cent. water of crystallisation, is very soluble in water, slightly soluble in alcohol of 83 per cent.

The *calcium-salt*, $C^{14}H^{22}Ca''O^{12}.10H^2O$, occurs, as already observed, in cinchona-bark, and is precipitated by chloride of calcium from alkaline quinates, after adding alcohol and ammonia, and leaving the mixture to stand. It crystallises in rhomboïdal plates of about 78° and 112°, often becoming hexagonal by truncation of the two acute angles, and easily splitting into shining laminæ. It dissolves in 6 pts. of water at 16°, its solubility varying greatly according to the temperature; nearly insoluble in alcohol. Contains, according to Baup, 29·5 per cent. water of crystallisation, which it loses at 100° (calc. 30·3 per cent.); it suffers no further loss of weight at 120°.

The *strontium-salt*, $C^{14}H^{22}Sr''O^{12}.10H^2O$, crystallises in tables apparently isomorphous with the calcium-salt, but distinguished by their rapid efflorescence, and the nacreous aspect which they assume on exposure to the air. It dissolves in 2 pts. of water at 12°, and in a much smaller quantity of boiling water. Contains 27·95 per cent. water of crystallisation, of which it loses three-tenths by efflorescence.

The *magnesium-salt* is very soluble, and forms crystalline efflorescences like cauliflower-heads.—The *yttrium-salt* dries up to a gummy mass.

Quinate of Cadmium, $C^{14}H^{22}Cd''O^{12}$, forms dirty-white laminæ and small white crystalline needles, permanent at 180°, soluble in about 253 pts. of cold water.—The *cobalt-salt*, $C^{14}H^{22}Co''O^{12}.5H^2O$, separates from the dark-red solution, after it has been left for several days to dry up to a syrup and then diluted with water, in small red nodules, which quickly effloresce and assume a lighter colour. After drying over oil of vitriol, or in the air, it gives off 5 at. water at 150°, and becomes reddish-blue. Does not melt when burnt.

Quinates of Copper.—*α.* The *normal salt*, $C^{14}H^{22}Cu''O^{12}$, is obtained by mixing aqueous quinic acid in excess with hydrate or carbonate of copper, and cooling the resulting solution, or leaving it to evaporate, any portion of green basic salt that may be precipitated at the same time being removed, and the neutral salt crystallised from water containing quinic acid. It forms pale-blue laminæ or needles, which contain 5 at. water of crystallisation, and give off two-thirds of it in contact with the air: dissolves in about 3 pts. of cold water, the solution decomposing on standing, and more quickly when heated, with separation of a basic salt.—*β.* A *basic salt*, $C^{14}H^{22}Cu''O^{12}.Cu''H^2O^2.2H^2O$, or $C^7H^{10}Cu''O^6.2H^2O$, is obtained:—1. By decomposing the barium-salt with somewhat less than the equivalent quantity of cupric sulphate, and adding a few drops of baryta-water to the clear filtrate, which then, on standing or evaporating, deposits regular crystals.—2. By boiling aqueous quinic acid with excess of cupric hydrate, and precipitating the filtrate with ether-alcohol. In this mode of preparation, however, it is difficult to separate the sparingly soluble salt from the excess of cupric hydrate.—3. The salt is likewise formed in small quantity, with evolution of acetic acid, on evaporating a solution of calcic quinate with cupric acetate. Over oil of vitriol it gives off only its adhering water (Kremers), amounting to between 1 and 2·5 per cent. Between 100° and 120°, it gives off all its water of crystallisation (Liebig), and decomposes at a temperature above 140°. Dissolves in 1150 to 1200 pts. water at 18°.

The *ferric salt* is a yellowish-red gummy mass, easily soluble in water.

Lead-salts.—*a.* The *normal salt*, $C^{14}H^{22}Pb''O^{12}.2H^2O$, forms needle-shaped crystals soluble in alcohol and extremely soluble in water.—*β.* A *basic salt*, $C^{14}H^{18}Pb^4O^{12}$ or $C^7H^9Pb^2O^6$, is deposited as a white bulky precipitate on mixing an alkaline quinate with basic acetate of lead, or on adding a little ammonia to the boiling solution of the normal salt. It is insoluble in boiling water, soluble in basic acetate of lead, and quickly attracts carbonic acid from the air.

The *manganese-salt* crystallises in rose-coloured laminæ.—The *mercuric salt* is colourless, uncrystallisable, and yields on desiccation a yellowish-red residue, sparingly soluble in water.—The *nickel-salt* is a green, gummy, very soluble mass.

Silver-salt, $C^7H^{11}AgO^6$.—On adding nitrate of silver to an alkaline quinate, the mixture blackens, and quickly deposits metallic silver. The silver-salt may, however, be obtained by saturating a weak solution of the acid with recently precipitated carbonate of silver. The solution evaporated in a vacuum yields mammellated groups of crystals, which are perfectly white, but easily blacken when exposed to light.

The *zinc-salt*, $C^{14}H^{22}Zn''O^{12}$, resembles the cadmium-salt in appearance, but is very soluble in water.

QUINIC ETHER. *Ethylic Quinate*, $C^9H^{16}O^6 = C^7H^{11}(C^2H^5)O^6$, obtained by heating quinate of silver with ethylic iodide, is a yellow syrup, viscid at mean temperatures, mobile at 50°, having a bitter taste and aromatic odour, easily soluble in water and in alcohol, less soluble in ether. It appears to distil, partly without decomposition, between 240° and 250°, in a stream of carbonic anhydride, but a large portion of it is decomposed with intumescence at a temperature a little above 100°. Heated on platinum-foil, it first volatilises in white smoke, and ultimately burns away with a bright flame. (Hesse, Ann. Ch. Pharm. cx. 335.)

QUINICINE. $C^{20}H^{24}N^2O^2$. (Pasteur, Compt. rend. xxxvii. 111 and 166.)—An alkaloïd isomeric with quinine and quinidine, and produced by the molecular transformation of either of those bases. It is prepared similarly to cinchonicine (i. 971), by heating sulphate of quinine with a small quantity of water and sulphuric acid. The salt remains fused even after all the water has been expelled; and by three or four hours' heating in the oil-bath to 120°—130°, the whole mass is transformed into sulphate of quinicine, mixed with an extremely small quantity of colouring-matter.

Quinicine is insoluble in water, but very soluble in absolute alcohol and in spirit of ordinary strength. It is very bitter, possesses febrifugal properties, and is precipitated from its solutions by alkalis as a fluid resin. It turns the plane of polarisation to the right. It unites easily with carbonic acid, and expels ammonia from its compounds at ordinary temperatures. A solution of quinicine in aqueous racemic acid deposits at first chiefly the dextrotartrate, whilst the lævotartrate remains in the mother-liquor. Quinicine is coloured green by chlorine-water and ammonia, though less strongly than quinine. (Herapath.)

QUINIDE or *Quinic Anhydride*, $C^7H^{10}O^5 = C^7H^{12}O^6 - H^2O$.—Prepared by heating quinic acid to 220°—250°, dissolving the residue in boiling alcohol, and leaving the clarified solution to evaporate. When recrystallised from water, it forms small crystals resembling sal-ammoniac. It has an acid reaction, dissolves easily in water, sparingly in dilute alcohol, and in presence of certain bases is reconverted into quinic acid. (Hesse, Ann. Ch. Pharm. cx. 335.)

QUINIDINE. $C^{20}H^{24}N^2O^2$.—This base, isomeric with quinine, exists in certain cinchona-barks together with quinine and cinchonine. It was first observed in 1833, by Henry and Delondre (J. Pharm. xix. 633), in the quinoïdine of commerce, in which it exists, together with smaller quantities of quinine, cinchonine, and resin. Van Heijningen, however (Ann. Ch. Pharm. lxxii. 302), first separated it from this mixture in the pure state, and showed that it is isomeric with quinine. Its action on polarised light has been studied by Pasteur (Compt. rend. xxxvi. 26). Several of its double salts have been prepared and examined by Stenhouse (Proc. Roy. Soc. xii. 491).

Occurrence.—In cinchona-barks, especially in some of the yellow barks (Henry and Delondre). According to Howard (Pharm. J. Trans. v. 368), it occurs in certain varieties of *Cinchona condaminea*, more especially var. *pitayensis*; according to Henkel (N. Repert. Pharm. xiii. 200), in *Cinchona nitida*, together with cinchonine and a little quinine. The root-bark of *C. Calisaya* contains quinidine and a small quantity of quinine. The red bark of *C. officinalis*, *C. micrantha*, and *C. succirubra*, grown in the East Indies, and taken at the age of eighteen months or less, was found to contain 6 per cent. of alkaloïds, of which about 4 per cent. consisted of quinidine, cinchonidine, and quinine, and 0·9 per cent. of cinchonicine with traces of cinchonine (Howard). According to Pasteur, the quinidine of commerce is for the most part a mixture of true quinidine with a second base.

Preparation.—Commercial quinoïdine is dissolved in the smallest possible quantity of ether; the filtrate is freed from ether by distillation; the residue is dissolved in dilute sulphuric acid; the solution is decolorised by animal charcoal, and precipitated by ammonia; the washed precipitate is dissolved in ether; and the ethereal solution, mixed with one-tenth of its volume of alcohol of 90 per cent., is left to evaporate. It then deposits crystals of quinidine, which are purified by washing with alcohol. The mother-liquors saturated with sulphuric acid yield, first crystals of sulphate of quinidine, and afterwards of sulphate of quinine. Quinoïdine thus treated yields from 50 to 60 per cent. of quinidine. (van Heijningen.)

De Vrij (J. Pharm. [3] xxxi. 183, 369) dissolves commercial quinoïdine in the smallest possible quantity of alcohol, and neutralises the solution with aqueous hydriodic acid; whereupon crystals of hydriodate of quinidine, amounting to 23 per cent. of the quinoïdine employed, soon make their appearance.

Properties.—Quinidine separates from its hot ethereal or alcoholic solution in large transparent monoclinic prisms, which effloresce and become opaque when exposed to the air. They contain 2 at. = 10·8 per cent. water of crystallisation, which they give off between 110° and 130°. The anhydrous base melts at 160°, and solidifies in a resinous mass on cooling.

The composition of anhydrous quinidine is as follows:—

	Calculated.		Henry and Delondre.	van Heijningen. *mean.*	Stenhouse.
C^{20}	240	74·07	74·44	74·08	74·04
H^{24}	24	7·41	7·10	7·44	7·71
N^2	28	8·64	8·68	8·55	
O^4	32	9·88	9·78	9·93	
$C^{20}H^{24}N^2O^4$	324	100·00	100·00	100·00	

Quinidine (? crystallised) dissolves in 1500 pts. of cold and 750 pts. of boiling *water*; in 3·7 pts. of hot *alcohol* of ordinary strength; in 45 pts. of absolute alcohol, and 90 pts. of cold *ether* (van Heijningen). Its solution in absolute alcohol turns the plane of polarisation strongly to the right; [α] = 250·75° for the transition tint (Pasteur). This property distinguishes quinidine from quinine, which is lævorotatory.

According to Kerner (Zeitschr. Anal. Chem. i. 152), there are three varieties of quinidine—viz.: α. Slightly soluble in lukewarm ether, crystallising from alcohol in large slowly efflorescent prisms, forming a sulphate which dissolves in 180 to 300 pts. of cold water.—β. Much more soluble in ether; crystallises from alcohol in small needles; sulphate soluble in 10 to 110 pts. water, the solution yielding a pulverulent precipitate with iodide of potassium, whereas the sulphates of all other cinchona-bases, except quinine, yield oleo-resinous precipitates with iodide of potassium.—γ. Still more soluble in ether; the sulphate has the same solubility as that of the α modification.

Decompositions.—1. Quinidine *burns* on platinum-foil with an aromatic odour like that of melilot, and partly volatilises.—2. Quinidine-salts, when *heated*, are converted into salts of quinicine (p. 13). *Chlorine-water* and *ammonia* colour quinidine green, even in solutions containing only $\frac{1}{5000}$th of the alkaloïd (Pasteur; Herapath). In concentrated solutions a precipitate is formed, which is not the case with quinine (Herapath). *Chlorine-water, ferricyanide of potassium,* and *ammonia,* added in succession to salts of quinidine, produce a permanent bulky precipitate; whilst the same reagents produce, with salts of quinine, only a red coloration, which quickly disappears (Schwarzer, N. Jahrb. Pharm. xxiii. 348).—Quinidine forms with *iodine* and *sulphuric acid* a compound corresponding to sulphate of iodoquinine (p. 25).—Quinidine heated for half an hour with *iodide of ethyl,* forms hydriodate of ethylquinidine. (Stenhouse.)

Salts of Quinidine.—Quinidine forms mono- and di-acid salts, which resemble the salts of quinine, but are, for the most part, more easily crystallisable. The sulphates, the mono-acid hydrochlorate, and the oxalate exert a powerful action on polarised light (Herapath). These salts are in some cases more soluble than the corresponding salts of quinine, so that oxalic, acetic, and tartaric acids do not precipitate soluble quinidine-salts. The hydrochlorate and nitrate are more difficultly soluble. With excess of acid the salts are as highly fluorescent as those of quinine. The precipitate thrown down by ammonia in their solutions dissolves far less easily than quinine, but more easily than cinchonidine, in excess of ammonia. (Riegel.)

Acetate of Quinidine crystallises from its syrupy solution in fine transparent crystals.

The *hydrobromate* precipitated by bromide of potassium from the sulphate or hydrochlorate is soluble in 200 pts. water at 14°.

Hydrochlorates.—The *mono-acid* or *neutral salt*, $C^{20}H^{24}N^{2}O^{2}.HCl$, is obtained by dissolving the base in hydrochloric acid, or by precipitating a cold saturated solution of the sulphate with chloride of sodium, in crystals containing 1 at. water, which they give off at 120°. It dissolves easily in water and in alcohol (van Heijningen). The acid salt, $C^{20}H^{24}N^{2}O^{2}.2HCl$, is produced by exposing quinidine to the action of hydrochloric acid gas, 100 pts. of the base taking up 22·52 pts. of the acid (calc. = 21·91 pts.). Its aqueous solution yields large fine crystals. (van Heijningen.)

Chloro-aurate, $C^{20}H^{24}N^{2}O^{2}.2HCl.2AuCl^{3}$.—Pale-yellow precipitate, melting and turning brown when heated to 115°, or boiled with water. (Stenhouse.)

Chloromercurate, $C^{20}H^{24}N^{2}O^{2}.2HCl.Hg''Cl^{2}$.—White precipitate, separating from a solution in boiling alcohol in pearly laminæ. It melts under boiling water; dissolves slightly in cold, more easily in hot water, and especially in water containing hydrochloric acid, from which last solution it is occasionally deposited in the form of a resin. (Stenhouse.)

Chloroplatinate, $C^{20}H^{24}N^{2}O^{2}.2HCl.Pt^{iv}Cl^{4}.2H^{2}O$.—Precipitated immediately from cold concentrated solutions, in crystals after a while from hot or dilute solutions; decomposes at 200°, with an odour of white-thorn; dissolves with difficulty in water, either cold or boiling; gives off 4·86 per cent. water at 100°.

Chlorozincates.—Slightly acid solutions of chloride of zinc throw down from alcoholic quinidine a granular powder, slightly soluble in cold and in boiling water, easily soluble in dilute hydrochloric acid. The easily formed solution of the precipitate in alcohol of 50 per cent. yields crystals resembling calc-spar, and containing 26·7 per cent. of chlorine ($C^{20}H^{24}N^{2}O^{2}.2HCl.Zn''Cl^{2}$ = 26·65 per cent. Cl); when recrystallised, the compound gives up hydrochloric acid and chloride of zinc, and is ultimately transformed into large hexagonal tables and prisms. The latter contain 7·44 per cent. of zinc at 100°, and are, therefore, $2(C^{20}H^{24}N^{2}O^{2}.HCl).Zn''Cl^{2}$ (calc. = 7·58 per cent. zinc. (Stenhouse.)

Hydriodates.—The *mono-acid* or *neutral salt* is thrown down by iodide of potassium from sulphate or hydrobromate of quinidine, as a white granular precipitate, which dissolves in 1250 pts. water at 15°, and separates from a boiling saturated solution in small, white, very hard crystals (De Vrij). The *diacid salt* has a pale-yellow colour, and dissolves in 90 pts. water at 15°. (De Vrij.)

Nitrate.—Large, flat, shining crystals. (van Heijningen.)

Argento-nitrate, $C^{20}H^{24}N^{2}O^{2}.AgNO^{3}$.—An alcoholic solution of quinidine mixed with nitrate of silver solidifies to a mass of fine needles, which may be recrystallised from boiling water containing nitric acid. It then forms fine silky needles, having a silvery lustre when dry. When recrystallised from alcohol, it decomposes with separation of silver. (Stenhouse.)

Oleate.—Quinidine behaves like quinine (p. 21), with oleic acid and olive oil. (Attfield.)

Oxalates.—By neutralising oxalic acid with quinidine, a *neutral salt*, $2C^{20}H^{24}N^{2}O^{2}.C^{2}H^{2}O^{4}.H^{2}O$, is obtained in small brittle crystals, nearly insoluble in cold but freely soluble in boiling water (Stenhouse). According to van Heijningen, on the other hand, the salt thus obtained is an *acid salt* containing $C^{20}H^{24}N^{2}O^{2}.C^{2}H^{2}O^{4}.H^{2}O$.

Picrate.—A solution of quinidine in boiling picric acid deposits on cooling a resin, which does not crystallise by evaporation from solution in alcohol. (Stenhouse.)

The *succinate* forms pearly prisms. (Henry and Delondre.)

Sulphates.—The *neutral salt*, $2C^{20}H^{24}N^{2}O^{2}.H^{2}SO^{4}.6H^{2}O$, is very much like the corresponding quinine-salt, but more woolly. It dissolves at 10° in 350 pts. water, and in 32 pts. absolute alcohol. Gives off 12·6 per cent. water at 130° (calc. for 6 at. = 12·84 per cent.).

The *acid sulphate* is crystallisable and very soluble in water. (van Heijningen.)

Sulphate of Iodoquinidine.—When a dilute solution of di-acid sulphate of quinidine is heated to 70° or 80° with one-third or half its volume of alcohol, and a little tincture of iodine is added, long four-sided prisms of a deep garnet-red colour crystallise out. The crystals are purple-red by reflected and dark brown-red by transmitted light, and polarise light like the corresponding quinine-salt (p. 25). They dissolve in 121 pts. of cold and 31 pts. of boiling alcohol, from which they are precipitated by water in the form of a cinnamon-brown powder. They contain 32·76 per cent. C, 4·44 N, 3·98 H, 6·34 SO^{3}, and 39·73 I, corresponding, according to Herapath, to the formula $C^{38}N^{2}H^{19}O^{4}I^{3}.SO^{3}.HO$ + 5 aq.—Other and optically different crystals are obtained when tincture of iodine is dropped into a strong solution of di-acid sulphate of quinidine mixed with 30 or 40 volumes of alcohol at a temperature below 70°. (Herapath, Chem. Soc. Qu. J. xi. 139.)

Tannate of Quinidine.—Aqueous quinidine forms a white precipitate with tannic acid.

Tartrate of Quinidine.—Pearly crystals, obtained in the same way as the oxalate (van Heijningen). The dextro- and lævo-tartrates undergo the same transformation as the quinine-salts when heated. (Pasteur.)

Tartrate of Quinidine and Potassium.—Quinidine and cream of tartar yield crystals soluble in alcohol. (Henry and Delondre.)

Tartrate of Quinidine and Antimony, $C^{20}H^{24}N^2O^2.C^4H^5(SbO)O^6 = \left.\begin{matrix}(C^4H^4O^4)''\\ C^{20}H^{25}N^2O^2\\ SbO\end{matrix}\right\}O^2$. —1. Mono-acid tartrate of quinidine is boiled for some hours with freshly precipitated oxide of antimony, and the filtrate is left to evaporate.—2. Powdered quinidine is added to a cold saturated aqueous solution of tartar-emetic; the liquid is heated to boiling; and the excess of quinidine, together with the precipitated oxide of antimony, is separated by filtration from the solution of the double salt and neutral tartrate of potassium. Long slender needles, which, after drying in a vacuum, lose ½ to 1 per cent. of water at 100°. Dissolves slightly in cold, easily in hot water, and easily also in boiling alcohol, from which it crystallises. (Stenhouse.)

Ethylquinidine, $C^{22}H^{28}N^2O^2 = C^{20}H^{23}(C^2H^5)N^2O^2$.—Not known in the free state. The *hydriodate,* $C^{22}H^{28}N^2O^2.HI$, is obtained by heating quinidine with excess of ethylic iodide, and crystallises from boiling dilute alcohol in long silky needles, nearly insoluble in water. On removing the iodine by oxide of silver, and filtering, a bitter alkaline solution is obtained, which absorbs carbonic acid but yields no crystals. On decomposing the hydriodate with chloride of silver, and treating the filtrate with platinic chloride, *chloroplatinate of ethylquinidine,* $C^{22}H^{28}N^2O^2.2HCl.Pt^{iv}Cl^4$, is precipitated as a pale-yellow powder, which dissolves very slightly in water either hot or cold, more freely in hot dilute hydrochloric acid. (Stenhouse, Ann. Ch. Pharm. cxxix. 20.)

Sulphate of Iodethylquinidine is obtained in the same manner as the corresponding quinine-compound. (Herapath, p. 25.)

QUININE. $C^{20}H^{24}N^2O^2$. *Chinin.* The *cinchona resin* of the older chemists.—The memoirs cited under CINCHONINE (i. 973) relate also to quinine; see also Pasteur (Compt. rend. xxxvi. 26; xxxvii. 110, 162; Jahresb. 1853, p. 419; Schützenberger (Ann. Ch. Pharm. cviii. 347, 350; Jahresb. 1858, p. 369).—On quinine alone: Robiquet (Ann. Ch. Phys. [2], xvii. 316); Stratingh (Repert. Pharm. xv. 139); Pelletier (J. Pharm. xi. 249); Duflos (Berz. Jahresb. xxvii. 1, 110); Strecker (Ann. Ch. Pharm. xci. 155; Jahresb. 1854, p. 505).

This alkaloïd, the most important constituent of the true cinchona-barks, on account of its tonic and antifebrile properties, was first obtained, but in an impure state, by Gomez of Lisbon, and by Pfaff in 1811; Pelletier and Caventou, in 1820, succeeded in separating it from the other constituents of the bark, and examined many of its properties; and its composition was established by Liebig in 1838.

The proportions of quinine and of the other alkaloïds in various kinds of cinchona-barks, as determined by different analysts, have already been given in the article CINCHONA-BARKS (i. 970). The following table exhibits the average results of the several determinations of the quantities of quinine and cinchonine:—

1. Brown or Grey barks:		
Huanoco . .	0·4 per cent. quinine,	1·7 per cent. cinchonine.
Loxa . . .	0·35 „	0·34 „
Pseudoloxa . .	0·35 „	0·66 „
Huamalies . .	0·3 „	0·8 „
Jaen pallida .	0·56 „	0·60 „
2. Yellow or Orange barks:		
Royal or Calisaya bark.		
a. *plana* . .	2·2 per cent. quinine,	0·28 per cent. cinchonine.
b. *convoluta* .	1·1 „	0·42 „
Cinchona flava fibrosa	1·05 „	0·83 „
Cinchona flava dura	0·54 „	0·48 „
Pitaya . .	1·68 „	0·90 „
3. Red bark:		
Cinchona rubra .	0·91 per cent. quinine,	1·05 per cent. cinchonine.

According to M'Ivor, a covering of moss on the bark during its growth increases the percentage of the alkaloïds; and this observation has been confirmed by De Vrij, who found in a young bark covered with moss, 8·4 per cent. of alkaloïds.

The extraction of quinine and cinchonine from cinchona-barks, by treating the bark with a dilute acid, and precipitating with lime or carbonate of sodium, has been already described under CINCHONINE (i. 973); also the usual methods of separating the two, depending: *a.* On the greater solubility of sulphate of cinchonine in water, and the greater facility of crystallisation of the quinine-salt.—β. On the greater solubility of quinine in cold alcohol, and in ether. Thiboumery (J. Pharm. [3] xvi. 369) extracts the alkaloïds from the lime-precipitate with oil of turpentine or coal-oil, instead of alcohol; Herring uses benzene for the same purpose. These liquids dissolve the quinine, with very little cinchonine, and give it up again to dilute acids: they have the advantage of taking up less of the colouring-matter than alcohol does. When the alkaloïds have been precipitated by carbonate of sodium, hot fatty oils may also be used for the extraction. [For other methods, see *Gmelin's Handbook*, xvii. 266. For the quantitative estimation of the alkaloïds, in cinchona-barks, see the same work, xvii. 268; also this Dictionary, i. 968.]

Properties.—Quinine is precipitated by an alkali from the solutions of its salts, as a white curdy hydrate, porous and friable when dry, agglutinating when heated. By fusion in a vacuum, or by prolonged heating to 120°, it may be deprived of its combined water, leaving a white opaque mass, which has a crystalline surface and concentric radiated fracture, becomes strongly negatively electric when rubbed, and melts to a transparent liquid at a higher temperature.

Quinine is permanent in the air, inodorous, very bitter, and antifebrile. According to Robin (Compt. rend. xxxii. 650), it prevents putrefaction. It restores the blue colour of reddened litmus. In alcoholic solution it exerts a left-handed action on polarised light: $[\alpha] = -141{\cdot}33°$ at 25° for the red ray (De Vrij and Alluard, J. Pharm. [3] xlvi. 192); $= -121{\cdot}5°$ at 22·5° and $-129{\cdot}56°$ at 16°, weaker therefore in warm than in cold solutions. Acids increase the rotatory power; ammonia restores it to its original amount (Bouchardat, Ann. Ch. Phys. [3] ix. 213). For solutions of quinine in acetic or sulphuric acid, $[\alpha] = 287{\cdot}16°$ at 24° for the transition-tint; therefore 220·15° for the red ray. (De Vrij and Alluard.)

The composition of anhydrous quinine is as follows:

	Calculation.		Pelletier and Dumas.	Regnault.	Liebig.	Laurent.	Strecker.
C^{20} . .	240	74·07	75·02	73·38	74·09	73·41	74·05
H^{24} . .	24	7·41	6·66	7·65	7·57	7·10	7·50
N^{2} . .	28	8·64	8·45	8·55			
O^{2} . .	32	9·88	9·87	10·42			
$C^{20}H^{24}N^{2}O^{2}$	324	100·00	100·00	100·00			

Pelletier and Dumas gave the formula $C^{20}H^{10}NO^{2}$; Regnault $C^{11}H^{23}N^{2}O^{4}$; Laurent $C^{38}H^{22}N^{2}O^{4}$ or $C^{19}H^{22}N^{2}O^{2}$. The correct formula was deduced from Liebig's analyses.

Quinine forms two hydrates, containing respectively one and three atoms of water.

a. *Trihydrate*, $C^{20}H^{24}N^{2}O^{2}.3H^{2}O$.—This is the ordinary hydrate obtained by precipitation. When a dilute solution of quinine-sulphate mixed with excess of ammonia is left to evaporate, slender needles, consisting of the same hydrate, gradually form on the surface; when dried, however, they present the appearance of an amorphous powder. A solution of quinine in absolute alcohol leaves on spontaneous evaporation a resinous mass, containing a few needles of the trihydrate, but it does not crystallise readily from alcohol; the ethereal solution of quinine leaves nothing but a resinous mass.

β. *Mono-hydrate*, $C^{20}H^{24}N^{2}O^{2}.H^{2}O$.—When the amorphous trihydrate freshly precipitated and washed is exposed to the air and frequently moistened, it is slowly transformed into crystals of the mono-hydrate, which dissolve in warm alcohol, crystallise again on cooling, and give up their water at 130° (Van Heijningen, Jahresb. 1849, p. 374). This hydrate constitutes Van Heijningen's *γ-quinine*. It dissolves less easily than ordinary quinine in alcohol, and is said to form a neutral sulphate different from the ordinary salt. De Vrij (N. Jahrb. Pharm. xiv. 268) did not succeed in preparing it.

Quinine dissolves in 364 pts. of cold *water* (Duflos); in 480 pts. *water* at 18·75° (Abl); in 200 pts. of boiling water (Pelletier and Caventou); 267 pts. (Duflos). It is very soluble in *alcohol*, and dissolves in *ether*, much more easily than cinchonine. It dissolves also in *volatile oils, fixed oils*, and *chloroform*. It is not quite insoluble in aqueous *alkalis*, especially when recently precipitated from its salts. According to Duflos, however, it is precipitated from aqueous solution by alkalis and alkaline carbonates, so that the presence of acids probably influences its solubility. It dissolves in 2,146 pts. of *lime-water*. (Calvert.)

Decompositions.—1. Quinine when strongly heated in the air turns brown, burns with flame, evolving an aromatic odour, and leaves a bulky easily combustible charcoal. —2. Solutions of quinine-salts turn brown in *sunshine*.—3. They are violently acted upon by the *electric current* (Hlasiwetz and Rochleder).—4. With aqueous *nitrite of potassium*, sulphate of quinine evolves nitrogen, and is converted into oxyquinine

(Schützenberger, iv. 320).—5. A solution of quinine in strong *nitric acid* becomes coloured on heating (Riegel), without forming picric acid (Liebig).—6. A solution in oil of vitriol immediately colours *chromate of potassium* dark-green, with evolution of gas (Riegel and Eboli).—7. *Permanganate of potassium* acts upon quinine in the cold, and more completely at boiling heat, forming carbonate and nitrate of potassium, and a peculiar acid (Cloez and Guignet, Compt. rend. xlvii. 710).—8. *Peroxide of lead* colours a solution of quinine in sulphuric acid grey-brown (Riegel). When a solution of quinine-sulphate is boiled with peroxide of lead, and dilute sulphuric acid is gradually dropt into it, a red substance called quinetin, partly soluble in water, is produced. (Marchand, p. 9.)

9. In contact with *zinc* and dilute *sulphuric acid*, quinine takes up 1 at. of water, and is converted into hydroquinine, $C^{20}H^{26}N^2O^3$ (Schützenberger).—10. When heated to 240° or 260° with *water* in a sealed tube, it forms chinoline. (Reynoso, Compt. rend. xxiv. 795.)

11. The solution of quinine in *oil of vitriol* acquires a yellowish-brown colour when heated (Riegel); *fuming sulphuric acid* colours quinine yellowish-green (Schliekenkamp), forming quinine-sulphuric acid (Schützenberger).—Salts of quinine heated alone, or with sulphuric acid and water, are converted into salts of quinicine (p. 13; Pasteur).

12. Quinine assumes a dirty-yellow colour in vapour of *iodine* (Donne). When triturated with iodine, it forms a brown compound, which appears to be identical with the precipitate formed on adding a solution of iodine in iodide of potassium to a quinine-salt. Quinine is decomposed by aqueous *periodic acid*, with liberation of iodine (Bödeker). When quinine, or its sulphate, is warmed with an equal quantity of *iodic acid*, an explosive evolution of gas takes place. (Brett, J. Pharm. [3] xxvii. 116.)

13. Quinine, *sulphuric acid*, and *iodine* together yield sulphate of iodoquinine (p. 25).

14. Quinine exposed to a current of dry *chlorine*, takes up a large quantity of the gas; according to André, it assumes a carmine-red colour in a few seconds, and becomes soluble in water; but according to Pasteur, it turns greenish, and then gives up to boiling or cold water only a small quantity of a substance having an acid reaction, whilst the remainder behaves like the body formed by the action of chlorine on quinine suspended in water. Quinine suspended in water is reddened by chlorine (André and Pelletier). A solution of quinine in 400 pts. of water, acidulated with sulphuric acid, is not coloured or rendered turbid on passing chlorine into it for ten minutes. (Lepage, J. Pharm. xxvi. 140.)

When *chlorine-water* and then *ammonia* are added to a solution of a quinine-salt, a green precipitate is produced, which is dissolved by more ammonia to a fine emerald-green liquid. Exact neutralisation of the liquid colours it a sky-blue, changing to violet or fiery-red on further addition of acid; ammonia restores the green colour (André, J. Pharm. xxii. 132). In this way [especially by employing an ethereal solution (Leers)] mere traces of quinine may be recognised; quinidine, however, exhibits the same reaction.

The green colour is not produced by other alkalis instead of ammonia. It is not produced when the chlorine-water is allowed to act too long, nor with all proportions of chlorine-water and ammonia; since with too little chlorine-water, ammonia throws down a greenish-white precipitate, and with too much it produces a yellow coloration (Brandes). Reddish-green or brown colours may also be produced. (André.)

When 200 grains of sulphate of quinine are dissolved in 80 ounces of chlorine-water, and the solution is mixed at once with 10 ounces of ammonia-water, a green precipitate is produced, amounting to about 60 grains, whilst the liquid remains of a deep-green colour. The precipitate is Brandes and Leber's *dalleiochine:* the colouring-matter of the solution is not removed by agitation with ether, nor in an unchanged state by other means, but splits up on evaporation into red *rusiochine*, soluble in alcohol, and dark-brown *melanochine*, insoluble in water and alcohol. (See *Gmelin's Handbook*, xvii. 272.)

15. When strong chlorine-water free from hydrochloric acid is poured into a concentrated solution of sulphate of quinine, till the liquid exhibits a faint yellowish colour, and finely pulverised *ferrocyanide of potassium* is then added till the colour changes to light rose-red, this tint gradually changes to dark-red, especially on addition of a larger quantity of the ferrocyanide. The red colour is not due to the formation of any cyanogen-compound, for it may be equally well-produced by means of baryta or lime-water, or of sodic borate or phosphate. (A. Vogel.)

16. When quinine is heated with strong *potash-ley*, hydrogen is evolved, chinoline (i. 869) distils over, and the residue appears to contain formic acid. (Gerhardt and Wertheim.)

17. With *iodide of methyl* and *iodide of ethyl*, quinine forms hydriodate of methyl- or

ethyl quinine (p. 25). With *chloride of acetyl* and *chloride of benzoyl* it yields the hydrochlorates of acetyl and benzoyl-quinine (p. 26).

Quinine-salts.—Quinine neutralises acids completely, forming *mono-acid* or *neutral* and *di-acid* salts. The salts are, for the most part, more easily crystallisable and less soluble in water than the salts of cinchonine. They have a strong bitter taste, and frequently exhibit a pearly or silky lustre. They are precipitated by *alkalis* and their *carbonates*, by the *hydrates of calcium* and *magnesium*, and by *ammonia* and *carbonate of ammonia*, hydrate of quinine being thrown down in white flocks. The precipitate produced by potash, ammonia, or carbonate of potassium is pulverulent, and not crystalline or soluble, to any great extent, even in excess of the precipitant; the sulphate alone yields a precipitate easily soluble in excess of ammonia (v. Planta). *Cyanide of potassium* colours quinine-salts carmine-red (Schwabe). *Lime-water* added in excess to quinine-salts redissolves the precipitate formed at first. Solutions of quinine-salts containing excess of acid are highly fluorescent.

Acetate of Quinine, $C^{20}H^{24}N^2O^2.C^2H^4O^2$, crystallises in long needles, which melt to a colourless glass. It gives off acetic acid at the heat of the water-bath, is slightly soluble in cold, very soluble in boiling water. (Regnault.)

The *arsenate* forms needle-shaped prisms resembling the phosphate, but less pearly.

The *aspartate* forms indistinct crystals, easily soluble in water.

Borate.—A hot solution of quinine in aqueous boric acid yields crystalline granules on cooling; by spontaneous evaporation with an excess of boric acid, a varnish is obtained.

Carbonate, $C^{20}H^{24}N^2O^2.H^2CO^3.H^2O$.—This salt is not formed by precipitation; but when quinine precipitated from the sulphate by ammonia is suspended in water, and carbonic acid is passed into the solution till the quinine dissolves completely, an alkaline liquid is obtained, from which crystals of carbonate of quinine are deposited on exposure to the air for twenty-four hours. By spontaneous evaporation of the mother-liquor, quinine is obtained free from carbonic acid. The carbonate forms translucent needles, having an alkaline reaction, efflorescing rapidly in the air, and decomposing at 110°, with liberation of carbonic acid; they are soluble in alcohol, but insoluble in ether. (Langlois, Ann. Ch. Phys. [3] xli. 89.)

The *chlorate*, formed by dissolving quinine in warm aqueous chloric acid, crystallises in tufts of slender needles, melting to a colourless liquid, which solidifies to a transparent varnish; it explodes when strongly heated. (Serullas, Ann. Ch. Phys. [2] xlv. 279.)

Chromates.—The *neutral salt*, $2C^{20}N^2H^{24}O^2.CrO^3$, is precipitated from an aqueous solution of neutral or acid sulphate of quinine by neutral chromate of potassium, in the absence of free acids, and is slowly deposited in tufts of shining golden-yellow needles, not affected by light, but assuming a green colour when heated above 92°. It dissolves in 2,400 pts. of water at 15°, in 160 pts. of boiling water; in alcohol, but not in ether. (André.)

The *acid chromate*, $C^{20}H^{24}N^2O^2.CrO^3.8H^2O$, is thrown down by acid chromate of potassium from a cold aqueous solution of sulphate of quinine containing sulphuric acid, as an orange-yellow precipitate, consisting of microscopic needles. It decomposes rapidly in the light, turns brown at 60° or 65°, or when boiled with water, evolving oxygen. More soluble than the neutral salt. (André, J. Pharm. [3] xli. 341.)

The *citrate*, $2C^{20}H^{24}N^2O^2.C^6H^8O^7$, is a sparingly soluble salt, crystallising in delicate needles.

Croconate and *Rhodizonate of Quinine* are deep yellow or red amorphous masses, soluble in water and alcohol (Heller).—The *cyanurate* is a white amorphous mass (Elderhorst).—The *formate* crystallises easily in needles resembling the sulphate. (L. L. Bonaparte, J. Chim. méd. xviii. 680.)

Gallate.—Gallic acid and alkaline gallates form precipitates with all salts of quinine, provided the solutions are not too dilute. The precipitate dissolves in boiling water, the liquid becoming milky and yielding an opaque deposit on cooling. Gallate of quinine is soluble in alcohol and in excess of acid (Pelletier and Caventou). According to Pfaff and Henry, gallic acid and alkaline gallates, when free from tannin, do not precipitate quinine-salts.

Hydriodate of Quinine, $C^{20}H^{24}N^2O^2.HI$, is obtained by direct union of the acid and base, or by double decomposition, in nodular groups of delicate crystals (Pelletier), lemon-yellow prisms (Herapath). A solution of sulphate of quinine in boiling water, mixed with an equivalent quantity of iodide of potassium, yields on cooling nothing but crystals of sulphate of quinine; but when 240 pts. of hydrochlorate of quinine are mixed with 460 pts. of iodide of potassium, in hot aqueous solution, a colourless turpentine-like mass is deposited as the liquid cools (Winckler). Iodide of potassium throws down from acetate or hydrochlorate of quinine, a heavy white powder, which runs into drops (v. Planta). The hydriodate melts to a resin over the water-bath. It dissolves in water more freely than the sulphate; in nearly all proportions in alcohol, and in ether (Winckler, Jahrb. pr. Pharm. xx. 321). From a solution containing excess of hydriodic acid, an *acid hydriodate*, $C^{20}H^{24}N^2O^2.2HI.5H^2O$, separates, according to Regnault, in large laminæ having a fine yellow colour and strong acid reaction.

By mixing acid sulphate of quinine with solution of iodide of potassium, Righini (J. Chim. méd. xiii. 116), obtained a red powder, containing, according to his analysis, 50 per cent. of quinine, 30 of hydriodic acid, and 20 of iodine, being a mixture of hydriodate of quinine and iodoquinine. According to Reignier (*ibid.* 119), on dissolving this precipitate in alcohol, and evaporating the solution, transparent four-sided prisms are obtained, which turn dull and brown-red in the air.

Hydrochlorates.—The *neutral salt*, $2(C^{20}H^{24}N^2O^2.HCl).3H^2O$, is easily obtained by dissolving quinine in a slight excess of warm dilute hydrochloric acid, and separates on cooling in long silky fibres. It may also be prepared by precipitating sulphate of quinine with chloride of barium, but the salt thus formed soon turns resinous in presence of an excess of hydrochloric acid (Winckler). At 140° in a current of dry air it gives off 7·105 per cent. water of crystallisation. An *acid hydrochlorate* separates from a solution of quinine in a large excess of hydrochloric acid; but on redissolving it in water, the solution deposits the greater part of the quinine as neutral hydrochlorate.

The neutral hydrochlorate forms yellow precipitates with *auric* and *iridic chlorides*.—The *chloromercurate*, $C^{20}H^{24}N^2O^2.2HCl.Hg''Cl^2$, is obtained as a granulo-crystalline precipitate, by dissolving equal parts of quinine and mercuric chloride in strong alcohol, and mixing the liquids after adding a little hydrochloric acid to the quinine-solution. If weak alcohol is used, the precipitate forms more quickly, but is less crystalline. It is very slightly soluble in water, cold alcohol, and ether.—The *chloroplatinate*, $C^{20}H^{24}N^2O^2.2HCl.Pt^{iv}Cl^4.H^2O$, is obtained by adding platinic chloride to a solution of quinine in a slight excess of hydrochloric acid, as a yellowish flocculent precipitate which on agitation becomes orange-coloured and crystalline, sinking to the bottom of the vessel and attaching itself to the sides. It does not give off any water at 100°, but the whole, equal to 2·37 per cent. (1 at.), at 140°. (Gerhardt.)

Hydrocyanate.—Quinine triturated and agitated with aqueous hydrocyanic acid dissolves to a yellow liquid.

Cyanoplatinates.—A solution of quinine-sulphate precipitated with platinocyanide of potassium yields the salt $C^{20}H^{24}N^2O^2.2HCy.Pt''Cy^2.H^2O$, and with platinidcyanide of potassium, the salt $C^{20}H^{24}N^2O^2.2HCy.Pt^{iv}Cy^4$ (Wertheim, Ann. Ch. Pharm. lxxiii. 210).—According to Schwarzenbach (Pharm. Viertelj. viii. 210), platinocyanide of potassium throws down:—*α*. From a solution of quinine in aqueous acetic acid, a white precipitate of the salt, $3C^{20}H^{24}N^2O^2.2HCy.Pt''Cy^2$, partly converted into needles on standing.—*β*. From a solution of quinine in a moderate excess of sulphuric acid, a bulky white precipitate, which when left at rest is transformed into tabular crystals containing $2(C^{20}H^{24}N^2O^2.2HCy.Pt''Cy^2)H^2O$, warty groups of needles consisting of $C^{20}H^{24}N^2O^2.2HCyPt''Cy^2.H^2O$, and a resin having the same composition.

Hydroferricyanate of Quinine, $2(C^{20}H^{24}N^2O^2.H^3Fe'''Cy^3)3H^2O$, is precipitated by a concentrated aqueous solution of ferricyanide of potassium from a strong aqueous solution of hydrochlorate of quinine containing a little free hydrochloric acid in golden-yellow crystalline laminæ, which after drying resembles mosaic gold. The salt does not lose weight at 100°; dissolves easily in water, and deposits a blue powder on evaporating the solution (Dollfus, Ann. Ch. Pharm. lxv. 224).—The *hydroferrocyanate*, $C^{20}H^{24}N^2O^2.H^4Fe''Cy^6.2H^2O$, is an orange-yellow crystalline precipitate, obtained on mixing the alcoholic solutions of quinine and hydroferrocyanic acid.

Hypophosphite, $C^{20}H^{24}N^2O^2.H^3PO^2$.—To prepare this salt, 100 pts. of sulphate of quinine are heated to 94° with 6,000 pts. of water and 38·7 pts. of hypophosphorous acid; a quantity of hypophosphite of barium, barely sufficient for the complete decomposition of the sulphate, is then added, and the liquid is filtered and left to crystallise. The mother-liquor and wash-water yield colourless crystals only when cautiously evaporated.—It is a light very loose mass, having a pure bitter taste; melts and turns brown at 150°, with loss of water; dissolves in 60 pts. of water at 15·5°, and more easily in boiling water. (L. Smith, Zeitschr. Ch. Pharm. i. 159.)

Hyposulphite of Quinine, $C^{20}H^{24}N^2O^2.H^2S^2O^3$ (at 100°), is obtained by adding hyposulphite of sodium to a solution of hydrochlorate of quinine, as a flocculent precipitate sparingly soluble in cold water. It crystallises from hot alcohol in fine needles containing 1 at. water, which they give off at 100°, yielding a powder, strongly electric when hot.—*Hyposulphate.*—Deposited in crystals from a hot solution of sulphate of quinine mixed with hyposulphate of barium. (Wetherill, Ann. Ch. Pharm. lxvi. 150; How, Ed. N. Phil. J. [2], i. 47.)

Iodates.—The *neutral salt* crystallises in moderately soluble silky needles; the *acid salt* is a sparingly soluble precipitate. (Serullas.)

Lactate of Quinine crystallises by spontaneous evaporation, in flat silky needles resembling the neutral sulphate, but more soluble. It is said to be efficacious in the treatment of intermittent fever. (L. L. Bonaparte.)

Mellitate.—Alcoholic quinine produces, with solution of mellitic acid, an abundant white precipitate, which becomes pearly and crystalline when washed with weak alcohol. It does not lose water at 100°, but evolves a little water and ammonia at 130°, turning sulphur-yellow; dissolves very slightly in cold, and somewhat more freely in hot water, from which it is deposited as a crystalline powder on cooling. (Karmrodt, Ann. Ch. Pharm. lxxxi. 170.)

Morintannate.—Pale-yellow precipitate, slightly soluble in water, easily in alcohol.

Nitrate, $C^{20}H^{24}N^2O^2.HNO^3$.—An aqueous solution deposits on evaporation oily drops, which turn waxy, and when kept under water for many days are transformed into very oblique rhombic prisms (Pelletier and Caventou). Crystals are obtained only by evaporating the excess of acid, and dissolving the residue in water (van Heijningen).—When neutral sulphate of quinine is decomposed by nitrate of barium, and the filtrate is allowed to evaporate spontaneously, large transparent prisms separate, which give off 4·2 per cent. of water at 100° (1 at. = 4·4 per cent.) (Strecker).—*Argento-nitrate.* Alcoholic nitrate of silver throws down, from alcoholic solution of quinine, a crystalline precipitate containing 1 at. silver-oxide to 1 at. quinine. (Strecker.)

Oleate.—Quinine is nearly insoluble in olive-oil, and does not saponify when heated with it. When 1 pt. of quinine is digested with 2 pts. of oleic acid for one to two hours at 100°, a solution miscible with fat oil is obtained (Attfield, Pharm. J. Trans. 1863, pp. 4, 388). By the action of quinine on olive-oil or *margaric acid*, Tripier (J. Pharm. [3], xlvi. 234) obtained soaps miscible in all proportions with oils and fats. The very viscid "*Oleomargarate de Quinine*" thus formed ultimately crystallises by slow cooling in shining globules.

Oxalates.—The *neutral salt*, $2C^{20}H^{24}N^2O^2.C^2H^2O^4$ (at 125°), is obtained by precipitating a cold solution of the acetate with oxalate of ammonium, washing the precipitate with a little cold water, and recrystallising from boiling alcohol, which deposits it on cooling in very fine needles.—The *acid salt* forms needles very soluble in water.

Perchlorate, $C^{20}H^{24}N^2O^2.HClO^4.7H^2O$.—When sulphate of quinine is precipitated by perchlorate of barium, and the filtrate is evaporated, yellowish oily drops are deposited, which redissolve on gently warming the liquid, and afterwards separate in crystals on cooling. By concentration, the mother-liquor yields a further quantity of oil, which solidifies in contact with a crystal.—According to Bödeker, the salt forms striated prisms, exhibiting a faint dichroïsm of blue and yellow; according to Dauber (Ann. Ch. Pharm. lxxi. 65), it forms truncated rhombic octahedrons, cleavable parallel to the end-face. P : P basal = 149° 46′; macrodiagonal = 80° 30′; brachydiagonal = 107° 32′. The crystals melts at 45°, and likewise at a moderate temperature over oil of vitriol; and the fused salt solidifies on cooling to a clear brittle mass, which loses 14·3 per cent. of water at 110°, puffs up strongly at 150°, and solidifies again at 160°, having then lost 18·63 per cent. of water. On further heating, a violent explosion occurs, accompanied by flame.—Aqueous solutions of a certain strength yield highly lustrous, dichroïc, rhombic tables, which melt to an oil under water, but only at 210° when heated alone, losing 6·5 per cent. of water (2 at. = 6·4 per cent.). (Bödeker.)

Periodate, $C^{20}H^{24}N^2O^2.HIO^4$.—Freshly precipitated quinine neutralises aqueous periodic acid but incompletely in the cold, and on warming the liquid, iodic acid is formed. When the acid solution is evaporated over oil of vitriol, it becomes covered with oily drops, which are converted into crystals as the evaporation proceeds. The periodic acid contained in the crystals is reduced on keeping for a short time, the crystals acquiring a yellow colour. On neutralising the alcoholic solution, and evaporating at 30° to 40°, roundish masses of needles are obtained. They dissolve easily in water containing nitric acid, but with difficulty in pure water, and after drying at 40° retain 9 at., and at 100°, 6 at. water. (Langlois, Ann. Ch. Phys. [3], xxxi. 274.)

Phosphates.—Quinine dissolves easily in warm aqueous phosphoric acid, and the solution on cooling yields a pulpy mass of needle-shaped crystals. A more dilute solution deposits radiated groups of very thin silky needles, perfectly neutral to test-paper. They give off 7·57 to 7·85 per cent. water at 120°, and probably consist of

$3C^{20}H^{24}N^2O^2.2PH^3O^4$ (Anderson, Ann. Ch. Pharm. lxvi. 59), or, according to Gerhardt (*Traité*, iv. 118), of $2C^{20}H^{24}N^2O^2.PH^3O^4.2H^2O$.—A hot solution of sulphate or hydrochlorate of quinine mixed with a slight excess of sodic phosphate, deposits on cooling a white crystalline mass, very slightly soluble in water. (Winckler.)

A *pyrophosphate of quinine* is obtained by precipitating the hydrochlorate with sodic pyrophosphate.

Picrate.—Obtained by precipitation as a yellow powder, very slightly soluble in water, freely in alcohol. When boiled in water, it melts and floats on the surface in oily drops (L. L. Bonaparte). According to Carey Lea (Sill. Am. J. [2] xxvi. 379), it crystallises from the alcoholic solution in yellow needles; according to L. Bonaparte, the alcoholic solution does not yield any crystals.

Quinate of Quinine occurs in cinchona-barks (Henry and Plisson). A solution of sulphate of quinine mixed with quinate of barium deposits the salt usually in mammellated crusts, having a horny appearance at the edges, sometimes, however, in needles. It dissolves in 3·5 pts. water at 110°, and in 8 pts. of alcohol of 88 per cent. (Baup.)

Succinate of Quinine forms pearly prisms.

Sulphates of Quinine.—*a. Neutral salt,* $2C^{20}H^{24}N^2O^2.H^2SO^4$, commonly but improperly called *Basic sulphate of quinine.* This salt is produced by neutralising quinine with dilute sulphuric acid, a few drops of alkali added to the solution quickly determining the crystallisation (see also p. 16). It crystallises in scales, or in long slightly flexible needles, having a nacreous aspect The crystals are monoclinic, exhibiting the combination $oP\ .\ \infty P\infty\ .\ [\infty P\infty]$. Angle $oP\ .\ [\infty P\infty] = 95°\ 50'$; $\infty P\infty : [\infty P\infty] = 90°$. They are often hemitropic. Cleavage distinct, parallel to oP and ∞P. The salt is as light as magnesia, has a bitter taste, and effloresces quickly on exposure to the air.

The sulphate dried in the air at 8° to 15°, or over oil of vitrol diluted with 3·2 to 3·5 its volume of water, has the composition $2(2C^{20}H^{24}N^2O^2.H^2SO^4).15H^2O$; the moist salt loses its excess of water when placed over acid of this strength, whilst the air-dried salt does not alter in weight. When heated to 110° to 120°, it loses the whole of its water of crystallisation, but rapidly absorbs 4·87 to 5·1 per cent. again on exposure to moist air (4 at. = 4·82 per cent.) (Jobst and Hesse); the same quantity of water is retained by the salt dried over oil of vitriol [or in dry air (Baup)]. A solution of 1 pt. of the air-dried salt in 40 pts. or more of alcohol of specific gravity 0·852, deposits on evaporation white needles, containing 4 at. water. (Jobst and Hesse, Ann. Ch. Pharm. cxix. 361.)

Commercial sulphate of quinine contains quantities of water varying between 5·1 and 13·3 per cent. (Millon and Comaille). It usually appears half-effloresced, but still contains 15·6 per cent. of water. (Guibourt.)

The anhydrous salt dissolves in 793 pts. water at 6°, and in 788 pts. at 9·5 (Jobst and Hesse). One part of the salt [crystallised or dry?] dissolves in 265 pts. of cold, and in 24 pts. of boiling water (Bussy and Guibourt); in 335 pts. cold, and 33 5 pts. boiling (Howard); in 720° pts. at 18·75° (Abl); in 740 pts. at 13°, and in 30 pts. at 100° (Baup); in 740 pts. at 10° (van Heijningen; Cap and Garot). The commercial salt dissolves in 738 to 770 pts. of water at 12° to 15° (Kerner). It dissolves very sparingly in a cold saturated solution of Glauber's salt, and scarcely at all in Rochelle salt, so that the solution is scarcely clouded by ammonia, or coloured by chlorine-water and ammonia (Mann). The solubility of sulphate of quinine in water is reduced by sulphate of sodium and sulphate of magnesium, but increased by sal-ammoniac, saltpetre, and chlorate of potassium. (Calloud.)

One part of anhydrous sulphate of quinine dissolves in 100 to 115 pts. of alcohol of specific gravity 0·852; the strength of the alcohol, however, is altered by the salt dissolved in it (Jobst and Hesse). One part of the salt [crystallised or dry?] dissolves in 60 pts. of cold alcohol of specific gravity 0·85 (Baup); in 60 pts. of cold alcohol of 21° (Delondre and Henry); in 40 pts. of alcohol (Cap and Garot); in 7·5 pts. of boiling alcohol of 90 per cent. (Bussy and Guibourt), from which it is deposited almost entirely on cooling. Sulphate of quinine dissolves in 40 pts. of glycerin, but not in fatty oils (Cap and Garot; Attfield). It dissolves abundantly in creosote at 20°, and slowly in cold picamar (Reichenbach). It is insoluble in chloroform. (Schlimpert.)

The solution of quinine-sulphate in water acidulated with sulphuric acid turns the plane of polarisation of a ray of light strongly to the left. For the transition-tint $[\alpha] = 255·6$ for the anhydrous sulphate, and 210·87° for the sulphate with 15·72 per cent. water (De Vrij and Alluard, Compt. rend. lix. 201). The same solution exhibits a powerful blue fluorescence. (See LIGHT, iii. 633.)

Sulphate of quinine becomes luminous at 100°; the phosphorescence is likewise produced by friction, the rubbing body becoming charged at the same time with negative electricity very sensible to the electroscope. The salt melts easily, forming a liquid like melted wax. At a higher temperature it assumes a fine red colour, and ultimately burns and carbonises.

Impurities and Adulterations of Sulphate of Quinine.—Sulphate of quinine may be intentionally adulterated, either with inorganic substances (such as sulphate or carbonate of calcium or magnesium), the presence of which is detected on heating, or with organic substances. Of the latter class of bodies, starch-powder and stearin are recognised by their insolubility in acidulated water, and gum by its insolubility in alcohol; salicin, phlorizin, and cane-sugar assume a red or brown colour with oil of vitriol; the other varieties of sugar, as well as other substances soluble in water, remain in solution on boiling the sulphate with baryta-water, passing carbonic acid into the liquid, and filtering, and may be recognised on evaporating the solution. The pure sulphate thus treated leaves only a slight residue, corresponding to the solubility of the salt in water.

Since cinchonine and cinchonidine exist, together with quinine, in cinchona-barks, the sulphates of those bases may occur as impurities in sulphate of quinine. They may be recognised by the following *quinine-test* of Liebig:—10 grains of the sulphate to be tested are warmed with 10 drops of dilute sulphuric acid and 15 drops of water in a test-tube; the solution is cooled; 60 drops of commercial ether and 20 drops of ammonia-water are added; the whole is shaken; and the tube stopped. If the quinine is free from cinchonine, and does not contain more than 10 per cent. of quinidine, the whole remains in solution; but if cinchonine is present, it is deposited as a white pulverulent layer between the ether and the water, as is also the case with cinchonidine when present in large quantity. Smaller portions of cinchonidine crystallise from the ether on standing for a short time, and still smaller quantities when ether saturated with cinchonidine is employed in the first instance. As it sometimes happens that the upper ethereal layer solidifies to a jelly, even with pure sulphate of quinine, it is more convenient to employ ether containing alcohol, or to take a somewhat larger proportion of ether than is directed above. Guibourt evaporates the ammonia before adding the ether (J. Pharm. [3] xxi. 47).—Instead of ether, Riegel (Jahrb. pr. Pharm. xxv. 340) employs 100 drops of chloroform, whereby the cinchonidine also is dissolved. To separate this last substance, he dissolves 10 grains of the sulphate in water, with addition of tartaric acid, and adds acid carbonate of sodium to the solution. The resulting precipitate consists of cinchonine and cinchonidine, whilst quinine remains in solution. The cinchonine and cinchonidine may then be separated by chloroform. O. Henry (J. Pharm. [3] xiii. 107) likewise separates quinine and cinchonine by means of ether or cold alcohol, but first removes the greater part of the quinine by converting it into acetate (by precipitating with caustic soda and dissolving the precipitate in acetic acid), and crystallising out as far as possible.—Delondre and O. Henry (J. Pharm. [3] xxi. 281) triturate 10 grms. of the sulphate and 4 grms. of acetate of barium with 60 grms. of water and a little acetic acid, separate the crystals which form after a few minutes, and dilute the filtrate with twice its volume of alcohol of 36°. After adding a little sulphuric acid and again filtering, the liquid is boiled with excess of ammonia, and after standing for 24 hours, the cinchonine crystallises in needles. The cinchonine may also be obtained in crystals by dissolving 5 grms. of the sulphate in 120 grms. of warm acidulated alcohol, boiling the solution with excess of ammonia, and setting it aside for 24 hours. (For references to other methods see *Gmelin's Handbook*, xvii. 280.)

β. Acid sulphate, $C^{20}H^{24}H^2O^2.H^2SO^4.15H^2O$, improperly called *neutral sulphate.*—This salt, which always separates from a solution of quinine in excess of sulphuric acid, is distinguished from the neutral sulphate by its much greater solubility. It usually crystallises on cooling in small needles, but by evaporation in a hot-air chamber, it may be obtained in rectangular prisms terminated by a truncation, or by two, three, or four facets resting on the faces of the prism.

It melts in its water of crystallisation at 100°, dissolves in 11 pts. of water at 13°, and in 8 pts. at 22°; and in dilute or absolute alcohol, much more freely in the hot liquids than in the cold. From a solution in absolute alcohol it is deposited in crystals, which immediately fall to powder on exposure to the air. (Baup.)

Sulphate of Quinine and Iron.—A mixture of sulphate of quinine and ferric sulphate, left for some months in a partially-covered vessel, deposits this salt in small, perfectly regular, colourless octahedrons. (Will, Ann. Ch. Pharm. xlii. 111.)

Sulphate of Iodoquinine (see p. 25).

Sulphite of Quinine.—Dry quinine absorbs sulphurous anhydride with considerable evolution of heat, forming an anhydrous salt. (Liebig and Pelouze.)

Sulphocyanate of Quinine, $C^{20}H^{24}N^2O^2.2CyHS$, obtained by precipitating a solution of quinine-sulphate with sulphocyanate of potassium, forms fine lemon-yellow monoclinic crystals (Wertheim). Quinine treated with sulphocyanic acid yields two salts crystallising together, the one white, the other yellow and resinous (Dollfus). By precipitating sulphocyanate of quinine with *mercuric chloride* and *cyanide*, two double salts are formed, containing respectively $3(C^{20}H^{24}N^2O^2.2CyHS).4Hg''Cl^2$ and $2(C^{20}H^{24}N^2O^2.2CyHS).Hg''Cy^2$. (Wertheim.)

Tannates.—Quinotannic acid occurs in cinchona-bark (Henry and Plisson). Gallotannic acid forms with dilute quinine-solutions a yellowish-white, amorphous, slightly bitter precipitate, sparingly soluble in boiling water, very soluble in alcohol. This salt is used in the treatment of fever, and is said to exert less action than the sulphate on the digestive organs and on the nervous system. (See *Report of MM. Orfila, Bussy, and Bouvier on a Memoir by M. Barreswil on the Therapeutic Properties of Tannate of Quinine*, J. Pharm. [3] xxi. 206.)

Tartrates.—*a. Dextrotartrates.* The *neutral salt*, $2C^{20}H^{24}N^2O^2.C^4H^6O^6$, is precipitated on mixing sulphate of quinine with neutral dextrotartrate of potassium, as a crystalline powder, neutral, fusible, and having a bitter taste (Arppe, J. pr. Chem. liii. 334). The *acid salt*, $C^{20}H^{24}N^2O^2.C^4H^6O^6.H^2O$, is obtained by mixing equivalent quantities of the acid and base, and leaving the liquid to crystallise. It gives off 1·4 per cent. water at 100°, and the remainder, 4·4 per cent. in all, at 160°, decomposing when heated for some time to that temperature (Pasteur).—*Tartrate of quinine and potassium* forms crystals soluble in alcohol (Delondre and Henry). Quinine boiled with solution of tartar-emetic does not form a double salt analogous to that of quinidine. (Stenhouse.)

β. Lævotartrate.—Obtained like the dextrotartrate, and has the same composition; it differs however in crystalline form, gives off nearly all its water of crystallisation at 100°, and is much more soluble in water than the dextrotartrate. (Pasteur.)

Urate of Quinine, $C^{20}H^{24}N^2O^2.C^5H^4N^2O^3$?—Prepared by boiling uric acid for some time with quinine and a large quantity of water, and filtering the liquid while hot; it is a white, amorphous, laminated mass (Elderhorst), or a dull white powder composed of microscopic prisms. It has a bitter taste; burns without melting when heated; dissolves in 855 pts. cold and 36·2 pts. boiling water; in 1580 pts. cold and 45·3 pts. boiling alcohol; still less freely in ether. (Andrea, Pharm. Viertelj. x. 382.)

Valerate of Quinine, $C^{20}H^{24}N^2O^2.C^5H^{10}O^2.\frac{3}{2}H^2O$.—On neutralising alcoholic quinine with a slight excess of valerianic acid, and allowing a mixture of 1 vol. of the liquid with 2 vols. of water to evaporate at ordinary temperatures, or not above 50°, hard rectangular octahedrons or cubes, permanent in the air, and by rapid evaporation also, needles are obtained (L. Bonaparte). The salt may also be prepared by adding carbonate of sodium to a mixture of 1 pt. of valerianic acid and 2 pts. of water in sufficient quantity to render the liquid slightly alkaline, and pouring the mixture, at a temperature of 48°, into a solution of 2 pts. of sulphate of quinine in water containing sulphuric acid: the solution, on standing for 24 hours, deposits crystals, which are washed with water at 36° (Chatin, J. Pharm. [4] i. 268). It smells of valerianic acid: tastes very bitter, and afterwards of the acid, melts at 90° to a transparent liquid, giving off 3½ per cent. of water, and solidifies to a glass on cooling. When more strongly heated, it gives off valerianic acid. The salt, fused at 90°, dissolves easily in alcohol, and remains on evaporation as an amorphous mass when the alcohol is strong, or in the form of crystals when weaker alcohol is employed. (Bonaparte.)

The crystals dissolve in 110 pts. of cold [96 pts. at 18·75° (Abl)], and in 40 pts. of boiling water (Wittstein). The solution on boiling deposits resinous drops of the anhydrous salt, which do not become crystalline on cooling or standing in water, but crystallise from dilute alcohol. The same anhydrous salt is precipitated by valerianic acid from an aqueous solution of the crystals (Bonaparte, J. Chim. méd. xviii. 680; xix. 330). Dissolves in 6 pts. of cold, and in 1 pt. of boiling alcohol of 80 per cent. (Wittstein, Repert. lxxxvii. 295). The salt prepared with natural, but not that made with artificial, valerianic acid, becomes phosphorescent when rubbed, especially after it has effloresced. The two salts also exhibit different crystalline forms. (Landerer, N. Br. Arch. cxix. 240.)

DERIVATIVES OF QUININE.

1. *By Addition.*

Hydroquinine, $C^{20}H^{26}N^2O^3 = C^{20}H^{24}N^2O^2.H^2O$ (at 150°) (Schützenberger, Ann. Ch. Pharm. cviii. 347).—This compound, which contains the elements of 1 at. water more than quinine, is obtained by the action of zinc and sulphuric acid on quinine. It is an amorphous resin nearly as bitter as quinine. When dried at 120°, It retains 1 at. water, forming the mono-hydrate $C^{20}H^{26}N^{2}O^{2}.H^{2}O$, which slowly gives off half its water at 140°, leaving the compound $2C^{20}H^{26}N^{2}O^{2}.H^{2}O$. The mono-hydrate softens at 35° and melts at 100°. Hydroquinine dissolves in alcohol and ether, and exhibits with chlorine-water and ammonia the same green coloration as quinine. Its salts are more soluble than the corresponding salts of quinine. The *sulphate* crystallises with difficulty. The *chloroplatinate* dried at 100° contains 26·2 per cent. platinum, agreeing exactly with the formula $C^{20}H^{26}N^{2}O^{2}.2HCl.Pt^{iv}Cl^{4}$.

Iodoquinine, $2C^{20}H^{24}N^{2}O^{2}.I^{3}$?.—By triturating quinine with iodine, a brown substance is obtained, exactly resembling iodocinchonine (i. 979), and containing 28·0 per cent. iodine (calc. = 30·3). (Pasteur, Compt. rend. xxxvii. 110.)

Sulphate of Iodoquinine, or *Sulphato-iodide of Quinine.* This salt, discovered by Herapath, is obtained by dissolving acid sulphate of quinine in strong acetic acid, and gradually dropping into it an alcoholic solution of iodine. The mixture, if left at rest for a few hours, deposits the salts in large plates, generally rectangular, sometimes rhombic, octagonal, or hexagonal. These crystals, when viewed by reflected light, exhibit an emerald-green colour, with an almost metallic lustre like the wing-cases of cantharides or the crystals of murexide; by transmitted light they are nearly colourless, having only a faint olive-green tint; but when two of them are placed across one another, so that their longest dimensions shall intersect at right angles, the superposed portions are quite impervious to light, just like two crossed tourmalines. This effect is produced even with crystals not thicker than $\frac{1}{20}$th of a millimetre. In polarised light, the crossed plates exhibit complementary colours, one for example being green and the other rose-coloured, and the superposed portions are of a dark chocolate-brown colour. In short, these crystals possess all the optical properties of tourmalines, and may be substituted for them, presenting moreover the advantage of transmitting a greater proportion of the incident light; but they are somewhat difficult to manipulate with, on account of their brittleness.

The composition of this salt has not yet been ascertained with certainty. Herapath originally assigned to it the improbable formula $C^{57}H^{33}N^{4}O^{5}I^{3}.2HSO^{4}.3HO$. His latest analysis, however, agrees better with the formula $2C^{20}H^{24}N^{2}O^{2}.3H^{2}SO^{4}.I^{6}$. Von Hauer's analysis, made in Kraut's laboratory, agrees nearly with same formula + $3H^{2}O$:

		Calc.	Herapath.			Calc.	v. Hauer.
C^{80}	960·0	40·81	41·35	C^{80}	960·0	39·89	39·39
H^{102}	102·0	4·34	4·70	H^{108}	108·0	4·48	4·67
N^{8}	112·0	4·76	3·54	N^{8}	112·0	4·64	
I^{6}	762·6	32·42	30·83	I^{6}	762·6	31·67	31·69
O^{11}	176·0	7·48	9·81	O^{14}	224·0	9·36	
$3SO^{3}$	240·0	10·19	9·77	$3SO^{3}$	240·0	9·96	9·98
	2352·6	100·00	100·00		2406·6	100·00	

—Herapath, Phil. Mag. [4], iii. 161; iv. 186: vi. 171, 346; vii. 352; ix. 366; xiv. 224; complete Chem. Soc. Qu. J. xi. 130; Chem. Gaz. 1858, p. 437; Jahresb. 1858, p. 364.—Haidinger and Stokes, Wien. Akad. Ber. x. 106; Jahresb. 1853, p. 198.—Gm. xvii. 312.

Sulphate of Iodethylquinine, prepared in like manner, forms either thin needles perfectly opaque, or thick plates, transparent and purple in thin films, and of a shining metallic green colour by reflected light, or dark-red or orange-red laminæ, transparent and orange-yellow by transmitted light.

Oxyquinine, $C^{20}H^{24}N^{2}O^{3}$.—Produced by boiling sulphate of quinine with nitrate of potassium, and precipitating by ammonia. Already described (iii. 320).

2. *By Substitution.*

Methylquinine, $C^{21}H^{26}N^{2}O^{2}$ = $C^{20}H^{23}(CH^{3})N^{2}O^{2}$. (Strecker, Ann. Ch. Pharm. xci. 164.)

When iodide of methyl is added to an ethereal solution of quinine, crystals of *hydriodate of methylquinine*, $C^{21}H^{26}N^{2}O^{2}.HI$, are formed in the liquid after standing for a while. The compound resembles hydriodate of ethylquinine in its behaviour with ammonia and caustic potash.

Ethylquinine, $C^{22}H^{28}N^{2}O^{2}$ = $C^{20}H^{23}(C^{2}H^{5})N^{2}O^{2}$. (Strecker, *loc cit.*)—Iodide of ethyl in contact with alcoholic or ethereal solution of quinine, forms, after some hours, yellow needles of hydriodate of ethylquinine, an aqueous solution of which is converted by oxide of silver into iodide of silver and a strongly alkaline solution of ethylquinine. When the latter is evaporated, and the amorphous residue is dissolved in alcohol and mixed with ether, a syrup is precipitated which is gradually converted into colourless needles, probably of hydrate of ethylquinine. The base tastes caustic and bitter in aqueous solution.—When heated to 120°, it evolves an odour of chinoline and decomposes. A strong alcoholic solution is not altered by iodide of ethyl.

Ethylquinine dissolves easily in *water* and in *alcohol*. It forms with *acids* mono- and di-acid salts. Aqueous ethylquinine absorbs carbonic acid from the air, and is converted into an uncrystallisable, alkaline salt.

Hydrochlorate of Ethylquinine, $C^{22}H^{28}N^2O^2.HCl$, or $C^{22}H^{24}N^2O^2.C^2H^5Cl$, crystallises in slender needles united in hemispherical groups.—The *chloroplatinate*, $C^{22}H^{28}N^2O^2.2HCl.Pt^{iv}Cl^4$, is a yellow precipitate, soluble in boiling water, and separating in indistinct crystals on cooling.

The *hydriodate*, $C^{22}H^{28}N^2O^2.HI$, or $C^{20}H^{24}N^2O^2.C^2H^5I$, when purified by washing with water, and recrystallising from ether, forms very light, colourless, silky needles, neutral, unchangeable at 110°, melting at a higher temperature, without loss of weight, and solidifying to a vitreous mass on cooling. Tastes very bitter. Dissolves freely in water, and is not precipitated by ammonia, but is thrown down in an unaltered state by a large quantity of caustic potash after standing for some time. Dissolves in alcohol, but not in ether.

The *neutral sulphate*, $2C^{22}H^{28}N^2O^2.H^2SO^4$, obtained by decomposing the hydriodate with sulphate of silver, is slightly soluble in water, more soluble in alcohol than the acid salt.

The *acid sulphate*, $C^{22}H^{28}N^2O^2.H^2SO^4$, crystallises in needles, which have an acid reaction, and after drying over oil of vitriol, give off 8·2 per cent. water (= 2 at.) at 120°. It is very soluble in water, less soluble in alcohol than the neutral sulphate. Potash added to the concentrated aqueous solution throws down a precipitate of the neutral sulphate, which dissolves in water.

Benzoyl-quinine, $C^{27}H^{28}N^2O^3 = C^{20}H^{23}(C^7H^5O)N^2O^2$. (Schützenberger, Compt. rend. xlvii. 334).—When chloride of benzoyl is poured upon quinine dried at 130°, an evolution of heat occurs, and the quinine deliquesces to a thick syrup, composed of hydrochlorate of benzoyl-quinine and excess of chloride of benzoyl. The syrup is dissolved in water; the base is precipitated by ammonia; and the white resinous mass is dried at 140°, at which temperature it gives off a large quantity of water.

Benzoyl-quinine is coloured green by *chlorine-water* and *ammonia*. The *platinum-salt* contains 23·2 per cent. of platinum (calc. for $C^{27}H^{28}N^2O^3.2HCl.Pt^{iv}Cl^4$ requires 23·5 per cent. Pt).

QUININE-SULPHURIC ACID, $C^{40}H^{48}N^4SO^7 = 2C^{20}H^{24}N^2O^2.SO^3$.—*Sulphoquinic acid.* Obtained by dissolving quinine in fuming sulphuric acid, neutralising with baryta, and decomposing the barium-salt with sulphuric acid. It is a solid amorphous acid mass, easily soluble in water and in alcohol.—The *barium-salt*, $C^{40}H^{46}Ba''N^4SO^7$, is a transparent friable vitreous mass having a bitter taste. (Schützenberger, Ann. Ch. Pharm. cviii. 353.)

Cinchonine forms a similar acid, containing $C^{40}H^{48}N^4SO^5$. (Schützenberger.)

QUINOA-SEEDS. See Chenopodium (i. 868).

QUINOÏDINE. This name is applied to the brown resinous mass obtained in the manufacture of quinine and cinchonine, by precipitating the brown uncrystallisable mother-liquor with ammonia or potash, or by evaporating the mother-liquors of sulphate of quinine to dryness. There appear to be two kinds of quinoïdine—the one freely soluble in ether, and containing quinidine, with smaller quantities of quinine, cinchonine, and resin; the other, which is only partially soluble in ether, consisting chiefly of uncrystallisable transformation-products of the cinchona-bases. The former is obtained from inferior kinds of cinchona-bark, but not from *Cinchona regia* or *C. flava dura*. (Winckler; see *Gmelin's Handbook*, xvii. 303.)

Animal quinoïdine.—This name is applied by Bence Jones and Dupré (Proc. Roy. Soc. xv. 73),to a fluorescent substance resembling quinine in optical and chemical properties, which may be extracted from every texture of man and of some animals, and is identical with the fluorescent substance existing in the crystalline lens.

QUINOÏL. An old name of Quinine.

QUINOLEINE. Syn. with Chinoline (i. 869).

QUINONAMIC ACID. Syn. with Quinoylamic Acid.

QUINONAMIDE. C^6H^5NO. (Woskresensky, J. pr. Chem. xxxiv. 251.)—A product intermediate in composition between quinone ($C^6H^4O^2$) and diphenine ($C^6H^6N^2$), formed by the action of dry ammonia or quinone:—

$$C^6H^4O^2 + NH^3 = C^6H^5NO + H^2O.$$

It is a crystalline mass of a fine emerald-green colour, soluble in water, but quickly decomposing, and yielding a nearly black solution.

QUINONE, $C^6H^4O^2$. (Woskresensky, Ann. Ch. Pharm. xxxvii. 168.—Wöhler, *ibid.*, li. 148.—Laurent, Compt. chim. 1849, p. 190.—Hesse, Ann. Ch. Pharm. xiv. 299.)—A compound produced: 1. By the oxidation of quinic acid. When quinic acid or a quinate is heated with about 4 pts. peroxide of manganese and 1 pt. strong sulphuric acid diluted with half its weight of water, the mass froths up, and gives off thick white vapours, which condense in the receiver to shining golden-yellow needles of quinone; the reaction is:

$$\underset{\text{Quinic acid.}}{C^7H^{12}O^6} + O^2 = \underset{\text{Quinone.}}{C^6H^4O^2} + CO^2 + 4H^2O.$$

The product is pressed between paper, and purified by sublimation. In like manner quinone may be obtained from coffee and other vegetable substances containing quinic acid (p. 9).—2. By the dry distillation of quinates.—3. From hydroquinone, by the action of heat (iii. 213).—4. From benzidine, aniline, and phenylene-damine, especially the β-modification (iv. 481), by oxidation with manganic peroxide and sulphuric acid. Benzidine thus treated yields a large quantity of quinone:

$$C^{12}H^{12}N^2 + H^2O + O^3 = 2C^6H^4O^2 + 2NH^3.$$

Aniline yields but a small quantity: $C^6H^7N + O^2 = C^6H^4O^2 + NH^3$, the greater part suffering more complete decomposition. (Hofmann, Proc. Roy. Soc. xiii. 4.)

Properties.—Quinone when sublimed forms long, transparent, golden-yellow, shining needles (Woskresensky); after crystallisation from hot water it is of a darker and dingier colour, and less transparent (Wöhler); from solution in hot ethylic iodide, it crystallises in beautiful laminæ (Hesse). It is heavier than water, melts at 100° (Woskresensky), at 115·7° (Hesse), to a yellow liquid, which crystallises on cooling (Wöhler), at 115·2° (Hesse). It volatilises without alteration, and sublimes, even at ordinary temperatures, from one part of the containing vessel to another. It has a pungent irritating odour. It is very slightly soluble in cold *water*, more soluble in *alcohol* and *ether*; the solutions have no effect on vegetable colours, but the aqueous solution colours the skin brown. It dissolves with yellow colour in dilute *hydrochloric* and *nitric acids*. The aqueous solution forms a pale-yellow gelatinous precipitate with *basic acetate of lead*, but does not precipitate the neutral salts of lead, copper, or silver.

Decompositions.—1. The aqueous solution of quinone acquires, by exposure to the air, a continually deeper yellowish-red colour, and ultimately deposits a black-brown mouldy substance (Wöhler). The aqueous solution mixed with ammonia or potash absorbs oxygen, and assumes a black-brown colour on exposure to the air, and then forms with acids a black mouldy precipitate, resembling melanic acid (iii. 867; Laurent, Compt. rend. xxvi. 35).—2. With dry *chlorine gas*, quinone forms trichloroquinone, the action being attended with great rise of temperature and evolution of hydrochloric acid (Woskresensky):

$$C^6H^4O^2 + Cl^6 = C^6HCl^3O^2 + 3HCl.$$

—3. Heated with hydrochloric acid and chlorate of potassium, it is quickly converted into tetrachloroquinone (Hofmann, Ann. Ch. Pharm. lxii. 65).—4. *Oil of vitriol* carbonises quinone (Woskresensky).—5. Strong *hydrochloric acid* colours quinone brownish-black, and then dissolves it, forming a red-brown afterwards colourless liquid, which no longer smells of quinone, but contains chlorohydroquinone, $C^6H^5ClO^2$. (Wöhler). The first products are probably quinhydrone and chloroquinhydrone (iii. 213, 217), the presence of both of which in the black magma formed at the begininng of the action was pointed out by Städeler (Ann. Ch. Pharm. lxix. 308):

$$4C^6H^4O^2 + 2HCl = C^{12}H^{10}O^4 + C^{12}H^8Cl^2O^4;$$

and these compounds, by the further action of the hydrochloric acid, are converted into chlorhydroquinone, being at the same time dissolved and decolorised:

$$C^{12}H^{10}O^4 + C^{12}H^8Cl^2O^4 + 2HCl = 4C^6H^5ClO^2.$$

Chlorhydroquinone is likewise formed by the action of hydrochloric acid gas upon dry quinone (Wöhler).—6. Quinone heated with *nitric acid* yields oxalic and picric acids. On treating it with nitric and strong sulphuric acids, and immersing metallic zinc in the diluted solution, a base is produced resembling aricine or cinchovatine (Schoonbroodt, Bull. Soc. Chim. 1861, p. 107).—7. *Ammoniacal gas* passed over quinone, quickly converts it, with separation of water, into quinonamide (p. 26).—8. *Sulphydric acid gas* has no action upon dry quinone, but when passed through the cold aqueous solution, first reddens it, and then throws down flakes of brown sulphohydroquinone, which, if the passage of the gas be still continued, and especially if the action be aided by heat, is converted into yellow sulphohydroquinone. The same compound is formed when sulphydrate of ammonium is poured upon quinone (Wöhler).—9. Quinone dissolved in water is converted into hydroquinone by excess of *hydriodic* or *hydrotelluric acid*, with precipitation of iodine or tellurium; and by *sulphurous acid*, with formation of sulphuric acid (Wöhler). *Sulphurous anhydride* has no action upon dry quinone; and even phosphuretted hydrogen, arsenetted hydrogen, and hydrocyanic acid are without action upon it (Wöhler).—10. *Quicklime*, or *hydrate of potassium*, in contact with moist crystals of quinone, acquires a fine indigo-blue colour; and on trituration a blue powder is formed, having a coppery lustre, and yielding a blackish-green solution with water (Hesse).—11. Quinone heated with hydrate of potassium is converted into quinonic acid, $C^{12}H^{8}O^{6}$ (Schoonbroodt, p. 30).—12. Quinone heated for a long time to 118° with *iodide of ethyl* in sealed tubes, yields long white crystals (Hesse).—13. With *aniline* in boiling alcoholic solution, it forms diphenyl-quinoyl-diamide. (Hofmann, iv. 430.)

Chloroquinones. When quinic acid or a quinate is heated with a mixture of peroxide of manganese, sulphuric acid, and common salt, a yellow crystalline sublimate is obtained, consisting of several chlorinated derivatives of quinone, which may be separated by their different degrees of solubility in alcohol. These compounds are more like quinone in proportion as they contain less chlorine, mono- and di-chloroquinone still crystallising in prisms, whereas tri- and tetra-chloroquinone crystallise in laminæ. By reducing agents, and especially by sulphurous acid, they are converted into the corresponding chlorhydroquinones (iii. 216).

Monochloroquinone, $C^{6}H^{3}ClO^{2}$ (Städeler, Ann. Ch. Pharm. lxix. 300). *Preparation.*—One pt. of quinate of copper, or any other quinate (25 grammes at most), is distilled with 4 pts. of a mixture of 3 pts. common salt, 2 pts. peroxide of manganese, and 4 pts. oil of vitriol (diluted with three times its bulk of water), in a flask provided with a descending tube six feet long, and kept cool at the upper part by a wet cloth, but not so much as to cause the liquid which distils over to crystallise. At first the mixture froths up considerably, giving off carbonic anhydride with a small quantity of chlorine; but when the liquid begins to boil, the evolution of chlorine ceases. The rapid ebullition must be kept up, as long as any oil passes into the receiver from the tube, in which, if it be moderately cooled, all the tetrachloroquinone is deposited. This oil, which solidifies on cooling, is collected on a filter, repeatedly washed with cold water, dried, pulverised, and exhausted with successive small quantities of cold alcohol of 85 per cent., as long as the alcohol acquires a yellow colour and gives a precipitate with water. Dichloroquinone then remains undissolved, together with a small quantity of tri- and tetra-chloroquinone, whilst the alcohol retains in solution the quinone and trichloroquinone, which colour it yellow. These compounds are precipitated from the solution, by addition of a triple volume of water, in slender needles and laminæ, and dissolved in a small quantity of hot moderately strong alcohol; the solution is cooled, till the large yellow laminæ of trichloroquinone, which separate out, begin to be associated with needles of monochloroquinone; the liquid is then immediately filtered and mixed with water; and the precipitate, consisting of monochloroquinone and a small quantity of trichloroquinone, is freed from the latter by repeatedly treating it as above with alcohol, which however cannot be effected completely, and is attended with great loss.

Monochloroquinone crystallises in long yellow needles, very soluble in *ether*, moderately soluble in *alcohol* and *acetic acid*. It dissolves also in boiling *water*, and separates on cooling; but if the boiling be prolonged, the solution becomes dark-red and opaque, with formation of brown chloroquinhydrone (iii. 217). Chloroquinone melts at 160° to a deep yellow oil, having an aromatic odour and biting taste. It colours the epidermis purple, like gold-salts. It dissolves in cold aqueous *sulphurous acid*, and is reduced thereby to chlorohydroquinone (iii. 216).

Dichloroquinone, $C^{6}H^{2}Cl^{2}O^{2}$.—This compound forms the portion of the oily product obtained in the preparation of monochloroquinone, which is but slightly soluble in alcohol. When purified by repeated crystallisation from hot alcohol, it forms shining, deep yellow, well-defined monoclinic prisms, melting at 160°, insoluble in *water*, nearly insoluble in cold *alcohol*, soluble in hot *alcohol*, very soluble in *ether*. It dissolves in weak *potash*, forming a red-brown solution, from which hydrochloric acid throws down prisms consisting of a peculiar acid.—Dichloroquinone dissolves slightly in *ammonia*, forming a yellow solution gradually changing to red and brownish-black. *Sulphuric, hydrochloric, nitric*, and *acetic acids* dissolve dichloroquinone, especially when hot, and deposit it in crystals on cooling. Sulphurous acid at the boiling heat converts it into dichlorohydroquinone or dichloroquinhydrone. (Städeler, *loc cit.*)

Trichloroquinone, $C^{6}HCl^{3}O^{2}$. (Woskresensky, J. pr. Chem. xviii. 419.—Städeler, Ann. Ch. Pharm. lxix. 318.)—Produced by the direct action of chlorine on quinone; also, together with the other chloroquinones, by the action above-mentioned. The action of chlorine on quinone is so violent at first, that the vessel requires to be kept cool at the beginning, but towards the end of the process it must be surrounded with boiling water. The product then volatilises with the vapours of hydrochloric acid, and is deposited in crystals on the cold parts of the apparatus; it may be purified by crystallisation from hot alcohol.

Trichloroquinone forms small yellow prisms melting at 160° and subliming at a lower temperature. It does not colour the skin, is quite insoluble in *water*, very soluble in *ether*, soluble in hot *alcohol*. Aqueous *potash* colours it green, and forms a brown solution, which gradually deposits long needles of a red salt, the acid of which is precipitated by hydrochloric acid in red needles.

Trichloroquinone is coloured green by strong aqueous *ammonia*, but the solution gradually assumes a brown-red colour, and yields by spontaneous evaporation hard dark-brown crystals.—*Sulphuric* and *nitric acids* dissolve trichloroquinone without alteration; *sulphurous acid* converts it into trichloroquinone.

The alcoholic solution of trichloroquinone does not precipitate acetate of lead or nitrate of silver.

Tetrachloroquinone, *Perchloroquinone*, or *Chloranil*, $C^6Cl^4O^2$. (Erdmann, J. pr. Chem. xxiii. 273 and 279; Hofmann, Ann. Ch. Pharm. lii. 55; Hesse, *ibid*. cxiv. 303.)—This compound is formed by the action of a mixture of hydrochloric acid and chlorate of potassium on quinone, aniline, phenol, trichlorophenol, dinitrophenol, trinitrophenol, salicin, salicylous acid, salicylic acid, nitrosalicylic acid, isatin, chlorisatin, dichlorisatin, and, according to Wagner (J. pr. Chem. lxvii. 441), on pyrocatechin; also, together with the other chloroquinones, when quinone is heated with peroxide of manganese, sulphuric acid, and common salt. (p. 28).

Preparation.—1. From *Phenol:* Strong hydrochloric acid is poured upon phenol in a basin; chlorate of potassium added in small crystals; and the mixture heated as soon as the first violent action is over, the heating being continued for some time, till in fact the phenol, which at first becomes thick and red-brown, is converted into a light yellow crystalline mass, which, after washing with water, may be crystallised from boiling alcohol. The transformation takes place more quickly when the phenol is dissolved in boiling water or in alcohol; but if alcohol be used, it is necessary, on account of the readiness with which explosion takes place, to use more dilute hydrochloric acid, and to add the chlorate gradually (Hofmann).—2. From *Salicin:* This substance is dissolved, together with chlorate of potassium, in boiling water; and small quantities of hydrochloric acid are added, whereupon the solution immediately acquires a deep orange-yellow colour, and becomes covered with a crust of small crystals of perchloroquinone, amounting to 30·27 per cent. of the salicin. If the salicin be first heated with hydrochloric acid alone, saliretin is formed, which, when afterwards heated with chlorate of potassium, does not yield any perchloroquinone (Hofmann).—3. *Quinone*, or the wash-water obtained in its preparation (p. 27), may also be boiled with hydrochloric acid and chlorate of potassium.

Properties.—Perchloroquinone forms pale-yellow scales, having a nacreous and metallic lustre. When gently heated, it sublimes completely without melting, but if suddenly heated, it melts, and suffers partial decomposition. It is insoluble in *water*, and nearly insoluble in cold *alcohol;* but dissolves in boiling alcohol, forming a pale-yellow solution, from which it crystallises on cooling in iridescent scales resembling iodide of lead. Ether dissolves it somewhat more readily than alcohol.

Perchloroquinone is not acted upon by hydrochloric, nitric, or ordinary sulphuric acid, even at the boiling heat (Erdmann), but dissolves without alteration in *fuming sulphuric acid*, and in a mixture of sulphuric and nitric acids (Hesse). *Sulphurous acid* converts it into tetrachlor-hydroquinone or chlorhydranil (Städeler). *Sulphurous anhydride* passed through a warm mixture of tetrachloroquinone and strong alcohol, forms octochlorinated ethyl-dihydroquinone (iii. 217), probably thus:

$$2C^6Cl^4O^2 + C^2H^6O + 3H^2O + 2SO^2 = C^{12}H^3(C^2H^5)Cl^8O^4 + 2H^2SO^4.$$

In like manner with *sulphurous anhydride* and *glacial acetic acid*, it yields octochlorinated acetyl-dihydroquinone (Hesse). A hot filtered solution of perchloroquinone in concentrated aqueous *acid sulphite of potassium* deposits crystals of thiochronate of potassium, $C^5H^4K^4S^4O^{14}$ (Hesse), thus:

$$C^6Cl^4O^2 + 4SHKO^3 + 2H^2O = C^5H^4K^4S^4O^{14} + 4HCl + CO^2.$$

A solution of tetrachloroquinone in concentrated *acid sulphite of ammonium* yields on cooling colourless crystals, consisting of the ammonium-salt of dichloro-disulphosalicylic acid, $C^6H^4Cl^2S^2O^7$, an acid which may be regarded as derived from sulphosalicylic acid ($C^6H^6O.CO^2.SO^3$), by the substitution of Cl^2 for H^2 and of SO^3 for CO^2 (Hesse). The maion of the ammonium-salt takes place as shown by the equation:

$$C^6Cl^4O^2 + 2SH(NH^4)O^3 + 2SO^2 + 3H^2O = C^6H^2(NH^4)^2Cl^2S^2O^7 + 2HCl + 2H^2SO^4.$$

Perchloroquinone heated to 100° in a glass tube, with dry *acetate of silver* and a little ether, yields chloride of silver and dichloroquinoylic acid; probably thus:

$$\underset{\substack{\text{Perchloro-}\\\text{quinone.}}}{C^6Cl^4O^2} + \underset{\substack{\text{Acetate of}\\\text{silver.}}}{2C^2H^3AgO^2} = 2AgCl + \underset{\substack{\text{Acetic an-}\\\text{hydride.}}}{C^4H^6O^3} + \underset{\substack{\text{Dichloroquinoylic}\\\text{anhydride.}}}{C^6Cl^2O^3}\ \text{(Hesse.)}$$

Perchloroquinone dissolves easily in hot dilute *potash* or *soda*, forming a purple liquid, which on cooling deposits dichloroquinoylate (chloranilate) of potassium or sodium (p. 34):

$$C^4Cl^4O^2 + 2H^2O = C^6H^2Cl^2O^4 + 2HCl.$$

It dissolves easily also in aqueous monosulphide of potassium, forming a yellow liquid, which in contact with the air quickly turns brown and finally black, and deposits a black granular powder. The recently prepared yellow solution yields, with hydrochloric acid, a yellowish-white precipitate, soluble in alcohol, ether, and caustic potash.

Perchloroquinone heated with aqueous ammonia is converted into dichloroquinoylamate of ammonium; with alcoholic ammonia it yields the same salt, together with dichloroquinoylamide (Laurent):

$$\underset{\substack{\text{Perchloro-}\\\text{quinone.}}}{C^6Cl^4O^2} + NH^3 + H^2O = \underset{\substack{\text{Dichloroquinoy-}\\\text{lamic acid.}}}{C^6H^3Cl^2NO^3} + 2HCl.$$

$$\underset{\substack{\text{Perchloro-}\\\text{quinone.}}}{C^6Cl^4O^2} + 2NH^3 = \underset{\substack{\text{Dichloroquinoyl-}\\\text{diamide.}}}{C^6H^4Cl^2N^2O^2} + 2HCl.$$

With *aniline* in presence of alcohol, perchloroquinone yields diphenyl-dichloroquinoyl-diamide. (Hofmann, iv. 426.)

QUINONIC ACID. $C^{12}H^8O^6$?—An acid obtained by Schoonbroodt (Bull. Soc. Chim. 1861, p. 107), by heating quinone with potash, but very imperfectly described. When heated with excess of potash, it is said to yield a brown empyreumatic oil, $C^{10}H^8O^2$, insoluble in water, and solidifying in the cold to brown crystalline laminæ. With the vapour of fuming nitric acid, this oil forms a nitro-compound insoluble in water; and from this, by the action of zinc and sulphuric acid, a colourless base is said to be obtained, soluble in alcohol, insoluble in ether, slightly soluble in water, and forming uncrystallisable salts, which have a sharp bitter taste, and yield with potash or ammonia a precipitate insoluble in excess of the reagent.

The name quinonic acid is also used as synonymous with quinoylic acid (p. 34).

QUINOTANNIC ACID, or *Cinchonatannic acid.* (Berzelius, *Lehrbuch*, 3 Aufl. vi. 246.—Pelletier and Caventou, Ann. Ch. Phys. [3] xv. 337.—R. Schwarz, J. pr. Chem. lvi. 76.)—Cinchona-barks contain a tannic acid different from gallotannic acid, which imparts to them the property of precipitating tartar-emetic greyish-yellow, colouring ferric salts green, and precipitating a solution of gelatin (Berzelius). The tannin, both from brown and from red cinchona-bark, precipitates ferric salts dark-green; that from yellow cinchona-bark forms a lighter green precipitate with ferric salts. (Pelletier and Caventou.)

Preparation.—The decoction of cinchona-bark is mixed with a small quantity of calcined magnesia, which precipitates cinchona-red; the filtrate is precipitated with neutral acetate of lead; the precipitate is decomposed under water by sulphydric acid; the liquid filtered from the sulphide of lead is precipitated with basic acetate of lead; the precipitate separated by filtration is dissolved in dilute acetic acid (which leaves cinchona-red undissolved); and the filtrate is precipitated by ammonia. The light-yellow precipitate is washed and decomposed by sulphydric acid, and the liquid filtered from the sulphide of lead is again precipitated by an alcoholic solution of neutral acetate of lead. If the quinotannate of lead thus obtained, be decomposed under water by sulphydric acid, and the liquid, filtered from the sulphide of lead, be evaporated in vacuo over oil of vitriol and a mixture of ferrous sulphate and lumps of potash, quinotannic acid remains behind, but already somewhat altered. (Schwarz.)

Quinotannic acid is a light-yellow, friable, very hygroscopic mass, which becomes electric by friction. Its taste is slightly sour and somewhat astringent, but not at all bitter. It dissolves in *water*, *alcohol*, and *ether*; the ethereal solution is nearly colourless. [The acid cannot be extracted from the bark by means of ether, because it is in combination with an alkali.] Schwarz found it to contain 44·75 per cent. carbon, 5·49 hydrogen, and 49·76 oxygen, whence he deduces the formula $C^{42}H^{30}O^{35}$.

Quinotannic acid subjected to dry distillation gives off an odour of phenol. Its aqueous solution rapidly absorbs oxygen from the air, especially in presence of fixed alkalis, acquiring a brown-red colour, and yielding cinchona-red (i. 969). A concentrated solution of the acid, boiled with a little hydrochloric acid, deposits red flocks, which dissolve with green colour in alkaline liquids (Schwarz). From the concentrated aqueous solution, hydrochloric and sulphuric acids throw down compounds of quinotannic acid with those acids, but less easily than from aqueous gallotannic acid.

Quinotannic acid unites with bases, forming salts which decompose in contact with the air, much more easily than the gallotannates, yielding cinchona-red and a carbonate. (Berzelius.)

With *starch, gelatin*, and *white of egg*, quinotannic acid reacts like gallotannic acid. It colours *ferric salts* green, and produces an abundant yellowish-grey precipitate with *tartar-emetic.* Its aqueous solution mixed with gallotannic acid dries up to a transparent varnish.

QUINOVA-BITTER. See QUINOVIN.

QUINOVA-SUGAR. $C^6H^{12}O^5$. (Hlasiwetz and Gilm, Ann. Ch. Pharm. cxi. 182; Jahresb. 1859, p. 581.)—A saccharine substance produced, together with quinovic acid, by the action of hydrochloric acid gas on quinovin in alcoholic solution (p. 32). It remains in the acid mother-liquor from which the quinovic acid has crystallised out, and may be separated by quickly neutralising the liquid with anhydrous carbonate of sodium or carbonate of lead, filtering, washing the precipitate with a small quantity of absolute alcohol, then distilling off the alcohol, evaporating to dryness at 100°, treating the residue with water, evaporating again, and exhausting the residue with absolute alcohol. The alcoholic solution thus obtained leaves the quinova-sugar, on evaporation, as an uncrystallisable hygroscopic mass, having a faint and slightly bitter taste. It emits an odour of caramel when heated, gives off a little water when exposed for some time to a temperature of 100°, reduces an alkaline cupric solution only when concentrated. It resembles mannitan more than any other kind of sugar.

QUINOVATANNIC ACID. A tannic acid obtained by Hlasiwetz (Ann. Ch. Pharm. lxxix. 130; Gm. xv. 484), from the bark of *Cinchona nova* or *C. surinamensis.* It is very much like quinotannic acid, but differs from the latter in having a somewhat bitter taste, and in not giving a precipitate with gelatin or tartar-emetic. It yielded by analysis 51·8 per cent. carbon and 5·8 hydrogen, whence Hlasiwetz deduces the formula $C^{28}H^{19}O^{17}$, requiring 52·01 C, 5·9 H, and 42·1 O.

QUINOVATIC ACID. See QUINOVIN.

QUINOVIC ACID. $C^{24}H^{38}O^4$. (Hlasiwetz and Gilm, Ann. Ch. Pharm. cxi. 1829; Jahresb. 1859, p. 579.)—This term was originally used as a synonym for quinovin or quinova-bitter, but is now applied by Hlasiwetz to an acid produced, together with quinova-sugar, by the decomposition of quinovin.

When dry hydrochloric acid gas is passed into a solution of quinovin in strong alcohol, the liquid becomes hot, and deposits quinovic acid as a white crystalline powder, while quinova-sugar remains in solution. The quinovin may be obtained pure by washing it with alcohol, then boiling it with a large quantity of strong alcohol, concentrating the solution by distillation, and leaving it to cool. The quinovin is then deposited as a white sandy powder composed of six-sided laminæ, belonging to the trimetric system. It is tasteless, insoluble in *water*, very slightly soluble in cold, and not very freely in boiling *alcohol*, sparingly soluble in *ether*. It has the properties of a weak acid, and dissolves easily in *alkalis;* but is precipitated from the ammoniacal solution by strong acids as a bulky gelatinous mass, which becomes pulverulent when left for some time under the liquid. The alcoholic solution is not coloured by ferric chloride.

Quinovic acid does not lose weight at 140°. When somewhat strongly heated on platinum-foil, it melts and solidifies to a fissured mass; at a higher temperature it gives off a vapour smelling like incense, and burns with flame, leaving no residue. By dry distillation it first gives off an oil smelling like oil of turpentine, then vapours having an odour of incense, and a thickish amber-yellow liquid, which condenses in the neck of the retort. It is scarcely affected by hydrochloric or even by boiling nitric acid; it dissolves in *sulphuric acid*, and is precipitated therefrom by water. When triturated, or warmed with *phosphoric chloride*, it liquefies, evolving hydrochloric acid, and on distillation, gives off phosphoric oxychloride, leaving a blackened residue.

Quinovates.—Quinovic acid is dibasic, the general formula of its salts being $C^{24}H^{36}M^2O^4$. It dissolves in alkalis and decomposes alkaline carbonates, but its ammoniacal solution gives off ammonia on evaporation. The same solution gives precipitates with salts of the heavy metals.—The *potassium-salt*, $2C^{24}H^{36}K^2O^4.3H^2O$ (at 160°), is obtained as a bulky pasty precipitate, on adding strong caustic potash to a concentrated ammoniacal solution of the acid, also by concentrating a solution of the acid in potash. —The *sodium-salt* resembles it, and is obtained in like manner.—The *barium-, strontium-*, and *calcium-salts* separate as gelatinous precipitates, on adding the corresponding chlorides to the ammoniacal solution of the acid.—The *copper-salt* is a light-blue precipitate, whose composition (at 120°) is approximately represented by the formula $C^{24}H^{36}Cu''O^4.5H^2O$.—The *silver-salt* is a bulky precipitate, quickly changing on exposure to light, and exhibiting when dried in a vacuum, and then at 120°, the composition $C^{24}H^{36}Ag^2O^4$.

QUINOVIN. $C^{30}H^{48}O^8$. *Quinova-bitter;* formerly also called *Quinovic, Quinovatic,* or *Chiococcic acid.* (Pelletier and Caventou, J. Pharm. vii. 112.—Winckler, Répert. Pharm. li. 193.—Buchner, jun. Ann. Ch. Pharm. xvii. 161.—Peterson, *ibid.* xvii. 165.—Schnedermann, *ibid.* xlv. 277.—Rochleder and Hlasiwetz, *ibid.* lxxvi. 238.—Hlasiwetz, *ibid.* lxxix. 129.—Schwarz, *ibid.* lxxx. 330.—Hlasiwetz and Gilm, *ibid.* cxi. 182; Jahresb. 1859, p. 578).—A substance discovered by Pelletier and Caventou in the false cinchona-bark of commerce (*Cinchona nova*), found also by Schwarz and by De Vrij (J. Pharm. [3] xxxvii. 256) in the true cinchona-barks. According to Rochleder and Hlasiwetz, quinovin (or perhaps rather quinovic acid) is formed by the action of acids and alkalis on caïncic acid (i. 710). It may be extracted from false cinchona-bark by boiling with milk of lime, precipitating the extract with hydrochloric acid, and purified by dissolving the precipitate in alcohol, reprecipitating with water, and repeating this operation till a perfectly colourless product is obtained. (Schnedermann.)

According to De Vrij, the crude quinova-bitter extracted from cinchona-bark may be separated by chloroform into quinovin, soluble in that liquid, and easily soluble in alcohol; and quinovic acid, insoluble in chloroform and only sparingly soluble in alcohol. He obtained quinova-bitter from all parts of *Cinchona Calisaya*, cultivated in Java: from the woody parts of the roots, 2·57 per cent.; from the root-bark, 1·08; from the wood of the stem, 1·80; from the bark of the stem, 0·36; from the bark of the woody branches, 0·68; from the herbaceous stalks, 0·85; and from the dried leaves, 0·23 per cent. The amount of quinova-bitter in the several organs (excepting the leaves, which contain no alkaloïds) is inversely proportional to the quantity of alkaloïds present.

Quinovin when dry forms amorphous fragments resembling gum. It has a very bitter taste, is nearly insoluble in *water*, moderately soluble in *ether*, very soluble in *alcohol*, and is not deposited from its solutions in the crystalline state (Schnedermann). It is soluble in *chloroform*, and turns the plane of polarisation of a luminous ray to the right, but less strongly than quinovic acid. (De Vrij.)

The analyses of quinovin (or quinova-bitter) by different chemists do not exhibit very close agreement, probably because some of the products examined consisted of crude quinova-bitter, containing quinovic acid as well as quinovin. Schnedermann found 67·2 per cent. carbon, 9·05 hydrogen; Hlasiwetz, 66·6 carbon and 8·9 hydrogen—numbers agreeing nearly with the formula $C^{30}H^{48}O^8$, which requires 67·2 carbon, 9·0 hydrogen, and 11·9 oxygen.

Quinovin yields by dry distillation a thick oil, having a strong odour of incense and petroleum, together with a small quantity of shining crystals. With *nitrous acid* it gives off red vapours; and on adding water to the solution, white amorphous flocks are precipitated, together with a resinous matter; no oxalic acid is produced.

When dry *hydrochloric acid gas* is passed into the alcoholic solution of quinovin, the latter is resolved into quinovic acid and quinova-sugar (Hlasiwetz):

$$C^{30}H^{48}O^8 + H^2O = C^{24}H^{38}O^4 + C^6H^{12}O^5.$$

QUINOYL. A diatomic radicle, which may be supposed to exist in quinone and its derivatives, quinone itself being regarded as the hydride $(C^6H^2O^2)''H^2$, dichloroquinone as the chloride of quinoyl $(C^6H^2O^2)''Cl^2$, a view which is in accordance with its reactions with alkalis (p. 28), and perchloroquinone in like manner as the chloride of dichloroquinoyl $(C^6Cl^2O^2)''Cl^2$.

QUINOYLAMIC ACID, $\left.\begin{array}{c}H^2\\(C^6H^2O^2)''\\H\end{array}\right\}\begin{array}{l}N\\O\end{array}$, is not known; but dichloroquinoylamic acid, $C^6H^3Cl^2NO^3 = \left.\begin{array}{c}H^2\\(C^6Cl^2O^2)''\\H\end{array}\right\}\begin{array}{l}N\\O\end{array}$, also called *dichloroquinonamic acid, chloranilam,* and *chloranilamic acid*, was discovered by Erdmann (J. pr. Chem. xxii. 287), and further examined by Laurent (Ann. Ch. Phys. [3] iii. 493). It is produced by the action of aqueous ammonia on perchloroquinone (chloranil):

$$C^6Cl^4O^2 + NH^3 + H^2O = C^6H^3Cl^2NO^3 + 2HCl.$$

The resulting red liquid, when concentrated, deposits crystals of dichloroquinoylamate of ammonium; and on mixing a saturated solution of this salt with hydrochloric or sulphuric acid, dichloroquinoylamic acid is deposited on cooling in black needles containing $2C^6H^3Cl^2NO^3.5H^2O$, having a fine adamantine lustre and often several inches long: it may be purified by crystallisation from boiling water.

Dichloroquinoylamic acid is slightly soluble in water, forming a violet solution, which precipitates metallic salts. Caustic potash decomposes it, eliminating ammonia, and forming dichloroquinoylate of potassium (p. 34). It is not altered by hydrochloric or sulphuric acid in the cold, but at the boiling heat these acids convert it into dichloroquinoylic acid.

Dichloroquinoylamate of Ammonium (or *Chloranilammon*) $C^6H^2(NH^4)Cl^2NO^3.2H^2O$, forms flattened chestnut-coloured shining needles, soluble with purple colour in water, especially when warm. The solution precipitates metallic salts.—The *barium-salt* is a light-brown precipitate, soluble with purple colour in hot water.—The *copper-salt* is a greenish-brown precipitate, obtained by mixing the ammonium-salt with cupric acetate.—The *lead-salt* is a red-brown precipitate; the *mercurous salt* a dark-brown precipitate. Mercuric chloride does not form a precipitate with the ammonium-salt.—The *silver-salt*, $C^6H^2AgCl^2NO^3$, is precipitated in brown flocks, often crystalline, and apparently easily decomposible.

QUINOYLAMIDES. 1. *Quinoyl-diamide*, $\left.\begin{matrix}(C^6H^2O^2)''\\ H^4\end{matrix}\right\}N^2$, is not actually known, but would probably be obtained by the action of ammonia on quinone in presence of alcohol, in the same manner as its derivatives, described below. Quinone treated with dry ammonia gas takes up 2 at. ammonia, and forms quinonamide, C^6H^5NO (p. 26).

Dichloroquinoyl-diamide, $\left.\begin{matrix}(C^6Cl^2O^2)''\\ H^4\end{matrix}\right\}N^2$. *Dichloroquinonamide, Chloranilamide* (Laurent, Rev. Scient. xix. 141).—This compound is formed by the action of ammonia on perchloroquinone (chloranil) in presence of alcohol:

$$(C^6Cl^2O^2)''Cl^2 + 4NH^3 = \left.\begin{matrix}(C^6Cl^2O^2)''\\ H^4\end{matrix}\right\}N^2 + 2NH^4Cl.$$

When a mixture of perchloroquinone, alcohol, and ammonia is gently heated, the liquid becomes red-brown, part of the solid substance dissolves (the solution containing dichloroquinoylate of ammonium), whilst another portion remains in the form of a brown-red precipitate. This precipitate is washed with alcohol, then redissolved in the liquid with addition of potash, and gentle heating; the liquid is filtered if necessary; and the potash is neutralised by an acid, while the liquid is still warm. Dichloroquinoyl-diamide is then separated almost immediately, as a red-brown precipitate, the colour of which is finer in proportion as the quantity of alcohol used is larger, and the temperature of the liquid higher. Too great a heat must however be avoided, as above a certain temperature the product would be decomposed by the potash.

Dichloroquinoyl-diamide in the dry state, is a crystalline powder composed of microscopic needles of a deep crimson colour and almost metallic lustre. It is insoluble in water, and nearly insoluble in alcohol and ether. When cautiously heated on a glass plate, it partly sublimes, partly decomposes. It is not attacked by hydrochloric acid, even at the boiling heat. It dissolves in strong sulphuric acid, forming a violet solution, from which it is almost wholly precipitated by water. Boiling potash eliminates ammonia, and converts the amide into dichloroquinoylate of potassium.

Diphenyl-quinoyl-diamide, $C^{18}H^{14}N^2O^2 = \left.\begin{matrix}(C^6H^5)^2\\ (C^6H^2O^2)''\\ H^2\end{matrix}\right\}N^2$, is produced by the action of quinone on aniline, in presence of a large quantity of boiling alcohol:

$$\underset{\text{Quinone.}}{3(C^6H^2O^2)''H^2} + \underset{\text{Aniline.}}{2(C^6H^5)H^2N} = \underset{\text{Diphenylquinoyl-diamide.}}{\left.\begin{matrix}(C^6H^5)^2\\ (C^6H^2O^2)''\\ H^2\end{matrix}\right\}N^2} + \underset{\text{Hydroquinone.}}{2C^6H^6O^2}.$$

The resulting brown solution deposits the diamide on cooling, in red-brown scales having an almost metallic lustre, and the mother-liquor evaporated with hydrochloric acid, yields a mixture of hydrochlorate of aniline and hydroquinone. (Hofmann, Proc. Roy. Soc. xiii. 4.)

Diphenyl-dichloroquinoyl-diamide, $C^{18}H^{12}Cl^2N^2O^2 = \left.\begin{matrix}(C^6H^5)^2\\ (C^6Cl^2O^2)''\\ H^2\end{matrix}\right\}N^2$.—This compound is produced by the action of aniline on perchloroquinone, according to the equation:

$$C^6Cl^4O^2 + 4C^6H^7N = C^{18}H^{12}Cl^2N^2O^2 + 2(C^6H^7N.HCl).$$

It was first obtained by Hesse (Ann. Ch. Pharm. cxiv. 292; Jahresb. 1860, p. 283), who regarded it as *dichloro-quinoyl-pentaphenyl-pentamide*; but Hofmann (*loc. cit.*) has shown that its true formula is that above given. It forms brown-black crystals, sublimable, insoluble in water and in cold alcohol, ether, hydrochloric acid, and alkalis, but soluble in benzene, by which it may be separated from another substance, formed in the same reaction. (Hesse.)

QUINOYLIC ACID, or *Quinonic acid,* $\left.\begin{matrix}(C^6H^2O^2)''\\H^2\end{matrix}\right\}O^2$, is not known, but its dichlorinated derivative has been obtained.

Dichloroquinoylic acid, $C^6H^2Cl^2O^4 = \left.\begin{matrix}(C^6Cl^2O^2)''\\H^2\end{matrix}\right\}O^2$.—*Dichloroquinonic acid, Chloranilic acid* (Erdmann, J. pr. Chem. xxii. 281).—Produced by the action of potash on perchloroquinone, dichloroquinoylamide, or dichloroquinoylamic acid. On adding hydrochloric acid to a solution of perchloroquinone in warm potash-ley, the liquid turns red, and deposits dichloroquinoylic acid in yellowish-white nacreous scales, which, when collected on a filter and viewed in mass, exhibit the colour of minium.

The crystallised acid contains 7·1 per cent. (= 1 at.) water of crystallisation, which it gives off at 115°; when heated in a test-tube it partly sublimes unaltered, but a considerable portion turns brown and decomposes. It dissolves in water, forming a violet solution, from which it is precipitated by sulphuric or hydrochloric acid.

Dichloroquinoylic acid is dibasic.

The *potassium-salt,* $C^6K^2Cl^2O^4.H^2O$, is deposited in crystals from a solution of perchloroquinone in warm caustic potash on cooling, and so completely that the mother-liquor retains only a very faint reddish or brownish tint. It is purified by recrystallisation from water. The crystals do not give off their water at 100°. The salt heated on platinum-foil burns with slight detonation, giving off purple vapours. It dissolves in water and alcohol, with purple colour, inclining to violet; less freely in potash. Its aqueous solution precipitates several metallic salts.—The *neutral ammonium-salt,* produced by the action of aqueous ammonia on perchloroquinone, crystallises like the potassium-salt.

The *barium-salt* is obtained by precipitation with chloride of barium, in red-brown micaceous scales, slightly soluble in boiling water. *Cobalt-salts, nickel-salts,* and *ferrous salts* are not precipitated by dichloroquinoylate of potassium.

Ferric dichloroquinoylate is a blackish precipitate, obtained with ferric nitrate. The *cupric salt* is a greenish-brown, the *lead-salt* a brown precipitate. The *mercurous salt* is a yellowish-brown precipitate obtained with mercurous nitrate. Mercuric chloride gives no precipitate.—The *silver-salt,* $C^6Ag^2Cl^2O^4$, is a brown-red pulverulent precipitate, which dissolves but very slightly in water, forming a reddish solution.

QUINTESSENCE. The alchemists distinguished four essences, answering to the four Aristotelian elements; to these Raimund Lullius added a fifth, namely alcohol, denominated *quinta essentia* on account of its enlivening action. The term is sometimes also used to denote the therapeutic constituents of any substance.

QUINTO. Prefix synonymous with PENTA.

QUIRINUS OIL. A kind of rock-oil or petroleum, of thickish consistence, so called from the Chapel of St. Quirinus, at Tegernsee, near which it issues. It is brownish-yellow, olive-green by reflected light, and has a specific gravity of 0·835.

R

RACEMIC ACID. $C^4H^6O^6 = \left.\begin{matrix}(C^4H^2O^2)^{iv}\\H^4\end{matrix}\right\}O^4$. *Paratartaric acid. Uvic acid. Traubensäure.*—An acid, isomeric with tartaric acid, but distinguished from the latter by several characters, and chiefly by its optical properties,—tartaric acid exhibiting the power of circular polarisation, whereas racemic acid is optically inactive, but may be separated into equal quantities of dextrotartaric and lævotartaric acids, exerting equal and opposite actions on polarised light. There is also a modification of tartaric acid, called *inactive tartaric acid,* likewise optically inactive, but not separable into the two optically opposite acids.

Racemic acid exists ready-formed in certain tartars, and was discovered in 1822 by Kestner, a manufacturer of tartaric acid at Thann, in the Vosges, who obtained it in large quantity from the tartars produced in the vintages of 1822–1824. It has since been found by Kestner and others in the crude tartars of Austria, Hungary, Saintonge, and especially of Italy, but never in such quantity as from those in which it was first discovered.

It is formed artificially by several processes:—1. By the direct combination of equal weights of dextrotartaric and lævotartaric acid.—2. By the action of heat on tartaric ether, and on the dextrotartrate or lævotartrate of quinine or cinchonine (Pasteur, Ann. Ch. Pharm. lxxii. 164, lxxxviii. 211).—3. By heating inactive tartaric acid to 200°, or by boiling it with hydrochloric acid (Dessaignes, Bull. Soc. Chim. 1865, i. 34).—4. From cane-sugar and other carbohydrates, and from mannite, dulcite, sorbin, mucic acid, and saccharic acid, by oxidation with nitric acid, sometimes alone, sometimes together with tartaric acid (Carlet, Rép. Chim. pure, ii. 345; iv. 17.—Hornemann, J. pr. Chem. lxxxix. 283; Jahresb. 1853, p. 380). The following are the relative quantities of tartaric and racemic acids produced by oxidation of different carbohydrates and of saccharic and mucic acids (Hornemann):—

	In 100 pts. of acid.	
	Tartaric.	Racemic.
Milk-sugar	55·4	44·6
Gum	63·0	37·0
Cane-sugar	59·7	40·3
Starch	100	. .
Dextroglucose	100	. .
Lævoglucose	. .	100
Saccharic acid	72·6	27·4
Mucic acid	?	100

Hornemann's experiments confirm the supposition of Liebig (Jahresb. 1859, p. 281) and of Heintz (*ibid.* 1860, p. 259), that the formation of tartaric acid from sugars by oxidation is preceded by that of saccharic acid, and the formation of racemic acid by that of mucic acid.

5. By boiling dibromosuccinate of silver with water (Perkin and Duppa, Chem. Soc. Qu. J. xiii. 102):

$$C^4H^2Ag^2Br^2O^4 + 2H^2O = C^4H^6O^6 + 2AgBr.$$

6. By heating an aqueous solution of racemo-carbonic (desoxalic) acid, or a dilute solution of its ethylic ether slightly acidulated with sulphuric acid, to 100° in a sealed tube for a considerable time: $C^5H^6O^8 = CO^2 + C^4H^6O^6$ (Löwig, Jahresb. 1861, p. 605). The acid obtained by the last two processes has not, however, been actually separated into dextro- and lævotartaric acid, so that it may possibly be inactive tartaric acid. The calcium-salt of the acid obtained from dibromosuccinic acid differs, also, in some respects from that of natural racemic acid. (Kekulé, p. 37.)

Preparation.—1. From crude tartar. Racemic acid accumulates in the mother-liquors obtained in the refining of tartar; and when these mother-liquors are treated with chalk, and the insoluble calcium-salt thus produced is decomposed by sulphuric acid, an acid liquid is obtained, which when concentrated yields crystals of racemic and tartaric acids. In most cases the tartaric acid forms the greater part of the product, and is deposited in large transparent crystals, the spaces between which are more or less filled up with small, white, opaque needles of racemic acid. By separating these needles, dissolving them in water, and evaporating, the racemic acid may be obtained in large crystals.

2. From tartrate of cinchonine.—This salt (either the dextro- or the lævotartrate), when subjected to a gradually increasing temperature, is first converted into tartrate of cinchonicine (i. 971); and if the heat be continued, the cinchonicine gives off water, and is transformed into cinchonidine, while the tartaric acid likewise undergoes alteration, and after exposure for five or six hours to a heat of 170°, is partly converted into racemic acid. To extract this acid, the black resinous mass is treated several times with boiling water; the filtered liquid is mixed with excess of chloride of calcium; the racemate of calcium thereby precipitated is decomposed by dilute sulphuric acid; and the filtrate is concentrated to the crystallising-point. (Pasteur.)

Part of the racemic acid formed in the process just described is further converted into inactive tartaric acid, the quantity of the latter increasing as the heating is prolonged; and if the solution obtained as above be filtered immediately after the addition of the calcic chloride, the inactive tartrate of calcium, which is more soluble than the racemate, remains in the mother-liquor, and separates after 24 hours quite free from racemate. By decomposing this salt with sulphuric acid as above, and concentrating the solution, the inactive tartaric acid may be obtained in crystals. Now Dessaignes has lately shown (Bull. Soc. Chim. 1865, i. 34), that this acid in the free state is partially converted by heat into racemic acid, although, when the latter is in combination with certain organic alkaloïds, the opposite transformation takes place. If the inactive tartaric acid, after being dried, be heated in a retort to 200°, till about a third of it has passed off in the form of volatile products, a distillate is obtained, consisting chiefly of pyroracemic acid (iv. 770), and the residue consists partly of racemic, partly of unaltered inactive tartaric acid. On dissolving this residue in water, and half neutralising with ammonia, acid racemate of ammonium crystallises out first, while the more soluble inactive tartrate, constituting about two-thirds of the whole, remains dissolved. Inactive tartaric acid may also be partly converted into racemic acid by boiling with hydrochloric acid.

Properties.—Racemic acid forms hydrated crystals, $C^4H^6O^6.H^2O$, belonging to the triclinic sytem. Dominant combination: $\infty{}'P$. $\infty\bar{P}\infty$. $\infty P{}'$. $\infty\breve{P}\infty$. $,\breve{P}'\infty$. $,\bar{P},\infty$. $'\bar{P},\infty$, sometimes with oP, $P{},$ and $,\breve{P}'\infty$. Angle $'\bar{P},\infty : \infty\breve{P}\infty = 128° 33'$; $'\breve{P}\infty : \infty\bar{P}\infty = 123° 32'$; $\infty{}'P : \infty,\breve{P}\infty = 110° 45'$; $\infty{}'\bar{P} : \bar{P}\infty = 129° 51'$; $\infty\bar{P}\infty : \infty P{},$ = 152° 54'; $\infty\breve{P}{}' : \infty\breve{P}\infty = 146° 30'$; $'\bar{P}'\infty : ,\bar{P}\infty = 111° 57'$; $'\bar{P}\infty : \infty P{}, = 113° 32'$; $\breve{P},\infty : \infty{}'\breve{P} = 107° 28'$; $'\bar{P}'\infty : \infty\breve{P}\infty = 84° 26'$; $'\bar{P}\infty : \infty,P = 120° 32'$. Ratio of axes, $a : b : c = 0·48434 : 1 : 0·80602$. Angle $\alpha = 120°$; $\beta = 96° 19'$; $\gamma = 76° 5'$. (De la Provostaye, Ann. Ch. Phys. [3] iii. 131.)

The crystals have a specific gravity of 1·690 (Buignet, Jahresb. 1861, p. 15): they effloresce slowly on exposure to the air, give off all their water of crystallisation at 100°, dissolve in 5·7 pts. water at 15°, and in 48 pts. cold alcohol of specific gravity 0·809. In these respects racemic acid differs considerably from tartaric acid, which forms anhydrous monoclinic crystals, much more soluble in water than those of racemic acid.

Towards reagents racemic acid behaves for the most part like tartaric acid. Its calcium-salt is, however, less soluble than the tartrate, so that racemic acid precipitates a solution of gypsum, whereas tartaric acid does not. Racemate of calcium is likewise insoluble in acetic acid, whereas the tartrate is soluble. On adding ammonia to a solution of calcic racemate in hydrochloric acid, a crystalline precipitate is formed in a few seconds; whereas with the tartrate, the precipitation does not take place for several hours.

Racemic acid when heated above 100°, remains unaltered up to 200°, and then yields the same products as tartaric acid; being converted, before complete decomposition takes place, into tartrelic acid, tartralic acid, and other products formed by abstraction of water, which, however, have not been completely investigated. (See TARTARIC ACID.)

When a solution of neutral racemate of ammonium is mixed with a small quantity of the soluble portion of beer-yeast, or an albuminous body, a vegetable extract, or any animal liquid, and exposed to a temperature of 30°, fermentation takes place, and the whole of the racemic acid is converted into lævotartaric acid (Pasteur, Jahresb. 1858, p. 248). The same transformation is produced when acid racemate of ammonium is fermented under the influence of *Penicillium glaucum*. (Pasteur, Jahresb. 1860, p. 250.)

Racemates. Racemic acid, like tartaric acid, is tetratomic and dibasic, the formulæ of the racemates containing monatomic metals being:

$$\text{Neutral Racemates } C^4H^4M^2O^6 = \left.\begin{matrix} H^2 \\ (C^4H^2O^2)^{iv} \\ M^2 \end{matrix}\right\}O^4.$$

$$\text{Acid Racemates } C^4H^5MO^6 = \left.\begin{matrix} H^2 \\ (C^4H^2O^2)^{iv} \\ HM \end{matrix}\right\}O^4.$$

With diatomic metals it forms only neutral salts, $C^4H^4M''O^6$.

The racemates are very much like the corresponding tartrates, but their crystalline forms are always holohedral, and their solutions exert no action on polarised light; whereas the tartrates are hemihedral, and exhibit circular polarisation (see LIGHT, iii. 675). Most of the racemates have been analysed by Fresenius (Ann. Ch. Pharm. xli. 1; liii. 230).

Racemates of Ammonium.—The *neutral salt*, $C^4H^4(NH^4)^2O^6$, obtained by spontaneous evaporation of a solution of the acid neutralised with ammonia, crystallises in rhombic prisms exhibiting the dominant combination, ∞P . $\infty\breve{P}2$. $\infty\breve{P}\infty$. P . $\bar{P}\infty$. $\frac{3}{5}\bar{P}\infty$. Angle $\infty P : \infty P = 99° 30'$; $\infty P : \infty\breve{P}2 = 160° 50'$; $\bar{P}\infty : \bar{P}\infty = 118°$; $\bar{P}\infty : \frac{3}{2}\bar{P}\infty = 169°$. Ratio of axes, $a : b : c = 0·5087 : 1 : 0·8466$. The crystals when exposed to the air become dull, and give off ammonia: they are very soluble in water, nearly insoluble in alcohol.—The *acid salt*, $C^4H^5(NH^4)O^6$, is precipitated as a crystalline powder, on neutralising 1 pt. of racemic acid with ammonia, and adding an equal quantity of the acid. It dissolves in 100 pts. water at 20°, and in a much smaller quantity of boiling water. It reddens litmus, and is insoluble in alcohol. From an aqueous solution slowly cooled, it crystallises in monoclinic prisms, often assuming the tabular form from predominance of oP. The decomposition of the racemates of ammonium by fermentation has been already described.

Racemate of Antimony.—White granular precipitate, obtained by adding alcohol to a solution of antimonious oxide in aqueous racemic acid. (Berzelius.)

Potassio-antimonious Racemate, $2C^4H^4(SbO)KO^6.H^2O$, is obtained by saturating a boiling solution of acid racemate of potassium with antimonious oxide, and crystallises on cooling from a saturated solution in monoclinic prisms terminated by the facets of a very obtuse octahedron. Observed combination, $\infty P \, . \, \frac{1}{3}P$. Angle $\infty P : \infty P = 85° \, 20'$; $\infty P : \frac{1}{3}P = 118° \, 2'$; $\frac{1}{3}P : \frac{1}{3}P = 140°$; the same behind $= 142° \, 55'$. Axes, $a : b : c = 1{\cdot}074 : 1 : 0{\cdot}9217$ (De la Provostaye). Like tartar-emetic, after drying at 100°, it loses 5·5 per cent. water at 260°.

Racemates of Arsenic and the Alkali-metals.—These salts are prepared by adding to a boiling solution of a neutral racemate of alkali-metal, first a small quantity of arsenious acid, then racemic acid, and so on alternately till a sufficient quantity of the double salt is produced, while a large excess of acid racemate of the alkali-metal remains in solution. On evaporating the liquid, the double salt and the acid racemate are deposited separately.—The *ammonium-salt*, $2C^4H^4(AsO)(NH^4)O^6.H^2O$, forms small efflorescent crystals, soluble in 10·6 pts. of water at 15°. Its solution is decomposed by evaporation into arsenious acid and acid racemate of ammonium.—The *potassium-salt*, $2C^4H^4(AsO)KO^6.3H^2O$, forms well-defined nacreous crystals, which effloresce and give off 4·23 per cent. water at 100°, the remainder of the crystallisation-water between 155° and 170°.—The *anhydrous salt* may be heated to 250° without alteration, but at 255° it gives off water and empyreumatic products. It dissolves in a very small quantity of hot water, but the solution is partially decomposed by evaporation, acid racemate of potassium being deposited, while arsenious acid remains in solution. The crystals dissolve in 7·96 pts. water at 16°.—The *sodium-salt*, $2C^4H^4(AsO)NaO^6.5H^2O$, forms large non-efflorescent crystals, which dissolve in 14·6 pts. water at 19°, give off $\frac{4}{5}$ths of their crystallisation-water at 100°, and the remainder at 130°. (Werther, J. pr. Chem. xxxii. 385.)

Racemate of Barium, $2C^4H^4Ba''O^6.5H^2O$.—Racemic acid forms with baryta-water, white flocks, which dissolve in excess of the acid; but the solution soon becomes turbid, and deposits the whole of the barium-salt as a crystalline precipitate. The same precipitate is formed on mixing racemate of sodium with chloride of barium.

Racemate of Calcium, $C^4H^4Ca''O^6.4H^2O$.—Obtained in the same manner as the barium-salt. Aqueous racemic acid also gives a precipitate after a while, with sulphate of calcium. Racemate of calcium assumes the form, either of an amorphous precipitate or of fine needles. The crystals give off their water (27·75 per cent.) at 200°. The salt is nearly insoluble in cold water, but dissolves in hydrochloric acid, and is precipitated therefrom by ammonia. It is insoluble in acetic acid, and likewise in excess of racemic acid, after it has become crystalline. The calcium-salt of racemic acid produced from dibromosuccinic acid (p. 35), crystallises from boiling water in cubic crystals containing $C^4H^4Ca''O^6.3H^2O$, whereas that of natural racemic acid separates from boiling water in small white prisms containing 4 at. water. The artificial calcic racemate, when dissolved in hydrochloric acid and precipitated by ammonia, likewise forms prisms with 4 at. water, but on recrystallisation from boiling water it assumes the cubic form with 3 at. water. The calcium-salt of the artificial acid is also somewhat more soluble in water than that of the natural acid. (Kekulé, Jahresb. 1861, p. 364.)

Racemates of Chromium.—The violet solution of chromic hydrate in racemic acid leaves on evaporation a violet crystalline mass soluble in water; alcohol added to this solution throws down a violet basic salt, which blackens in drying, and dissolves in water only on addition of racemic acid.—With *potash*, racemate of chromium forms a solution which leaves a dark-violet mass on evaporation, and is completely precipitated by lime-water.

Racemate of Cobalt.—The solution of recently precipitated cobalt-oxide in racemic acid, yields by evaporation a pale red crystalline crust, soluble in water containing racemic acid; it dissolves also in potash, forming a violet solution, which on dilution deposits a dingy-blue precipitate.

Racemates of Copper.—*a.* The *cuprous salt* is obtained by digesting cuprous oxide with racemic acid in a tightly-closed vessel. It is moderately soluble in water, and is deposited on cooling in colourless rhomboïdal prisms. When exposed to the air it is converted into the cupric salt.

β. Cupric Racemates.—A mixture of the hot solutions of racemic acid and cupric sulphate, deposits, after a while, pale-green tabular crystals. A dilute solution of cupric acetate forms with racemic acid pale-blue needles, containing $C^4H^4Cu''O^6.2H^2O$ This salt gives off its water at 100°, dissolves sparingly in water, easily in hydrochloric acid; the solution when mixed with potash assumes a fine blue colour, and is not decolorised even at the boiling heat. Alkaline racemates form a green precipitate with cupric salts.

Cupric racemate dissolves in caustic alkalis and alkaline carbonates. On adding alcohol to a saturated solution of the salt in caustic soda, dark-blue needle-shaped crystals are deposited on the sides of the vessel, and light-blue tables at the bottom; both consisting of the salt, $C^4H^4Na^2O^6.Cu''O.4H^2O$, sparingly soluble in cold, more soluble in boiling water, and depositing cuprous oxide when boiled with excess of alkali.

Racemates of Iron.—Ferric hydrate dissolves in racemic acid, an insoluble basic salt being formed at the same time. The solution when evaporated leaves a brown amorphous mass, easily pulverised, very soluble in water, not precipitable by alkalis.—With *potash*, ferric racemate forms a dark-brown, granular, deliquescent double salt, soluble in racemic acid.

Racemate of Lead, $C^4H^4Pb''O^6$ (at 100°).—On adding racemic acid drop by drop to a hot solution of lead-acetate as long as the precipitate redissolves, and cooling the filtrate, racemate of lead is deposited in shining grains or delicate needles, soluble in hot aqueous racemic acid.

Racemate of Magnesium, $C^4H^4Mg''O^6.5H^2O$.—A solution of magnesium-carbonate in the boiling aqueous acid deposits this salt on slow cooling in small right rhomboïdal prisms; by quick cooling or prolonged evaporation as a white powder. It effloresces in dry air, gives off 4 at. (27·24 per cent.) water at 100°, the rest without decomposition at 200°. It dissolves in 120 pts. water at 19°, in a small quantity of boiling water, is insoluble in alcohol, dissolves in racemic acid, but the solution deposits nothing but the neutral salt and the free acid.

A saturated solution of magnesium-carbonate in an acid racemate of alkali-metal yields by slow evaporation, a syrupy mass, which gradually changes on cooling to an amorphous double salt, from which water extracts but a small quantity of alkaline racemate, even at the boiling heat.

Racemate of Manganese, $C^4H^4Mn''O^6.H^2O$.—Obtained by evaporating a solution of manganous acetate mixed with racemic acid, in yellowish-white crystals, permanent in the air even at 100°, slightly soluble in water, easily soluble in acids and alkalis.

Racemate of Mercury.—Racemic acid forms with mercurous nitrate, a white heavy precipitate, which becomes coloured on exposure to light, is insoluble in water and in racemic acid, but soluble in nitric acid.

Racemate of Nickel, $C^4H^4Ni''O^6.5H^2O$, is obtained, like the manganous salt, in green needles, which effloresce slowly at ordinary temperatures, rapidly at 100°. It is but slightly soluble in pure water, more soluble in water containing racemic acid. It dissolves with green colour in potash, also in hot aqueous carbonate of sodium, the liquid solidifying to a gelatinous mass on cooling.

Racemates of Potassium.—The *neutral salt*, $C^4H^4K^2O^6.2H^2O$, crystallises by slow evaporation, according to Pasteur, in six-sided tables belonging to the trimetric system, and exhibiting the combination $oP \,.\, \infty\breve{P}\infty \,.\, \infty P$. Angle $\infty\breve{P}\infty : \infty P = 128° 20'$. According to v. Lang, on the other hand (Wien. Akad. Ber. xlvi. [2] 31; Jahresb. 1862, p. 305), the crystals (with the same amount of water) are monoclinic, exhibiting the combination $\infty P\infty \,.\, [\infty P\infty] \,.\, oP \,.\, [P\infty] \,.\, [2P\infty] \,.\, \infty P \,.\, \infty P\frac{5}{3} \,.\, -P \,.\, +P \,.\, +P2$. Axes $a : b : c = 1 : 0·9134 : 0·7586$. Angle of inclined axes $= 92° 35'$. $[P\infty] : [\infty P\infty] = 97° 9'$; $[2P\infty] \,.\, [\infty P\infty] = 146° 35'$; $[2P\infty] : oP = 122° 56'$, $\infty P : \infty P\infty = 137° 57'$; $\infty P : oP = 88° 6'$; $\infty P\frac{5}{3} : oP = 87° 43'$; $-P : oP = 132° 43'$. The crystals dissolve in 0·97 pt. water at 25°, are nearly insoluble in alcohol, and give off all their water at 100°. Mineral acids or racemic acid added to the solution throw down the acid racemate.—The *acid salt*, obtained like the corresponding ammonium-salt, forms crystals soluble in 180 pts. of water at 19°, in 139 pts. at 25°, and in 14·3 pts. of boiling water; it is insoluble in alcohol, but dissolves easily in mineral acids.

Racemate of potassium and ammonium, $C^4H^4K(NH^4)O^6$, is obtained by slow evaporation of a solution of the acid potassium-salt saturated with ammonia, in acicular, longitudinally striated, rhombic prisms, having the angle $\infty\breve{P}\infty : \infty P = 130° 45'$, and not modified at the ends. (Pasteur.)

A *racemoborate of potassium* is obtained, according to Fresenius, by evaporating a solution of 1 at. boric acid and 2 at. acid potassic racemate, at 100°, as a white, acid, almost crystalline, friable mass, very soluble but not deliquescent. Similar products are obtained by evaporating a solution of borax and acid racemate of potassium or sodium. (Fresenius.)

Racemate of Silver, $C^4H^4Ag^2O^6$.—When a warm moderately strong solution of the acid potassium-salt is added to a solution of silver-nitrate heated to 80° or 85°, till the precipitate begins to be permanent, the liquid on cooling deposits racemate of silver in fine shining scales, less soluble in water than the tartrate, soluble in ammonia.

Racemates of Sodium.—The *neutral salt*, $C^4H^4Na^2O^6$, crystallises readily in anhydrous rhombic prisms soluble in 2·63 pts. of water at 25°, insoluble in alcohol.—The *acid salt*, $C^4H^5NaO^6.H^2O$, is precipitated by alcohol from a mixture of equivalent quantities of the neutral salt and racemic acid, and may be obtained, by recrystallisation from water, in monoclinic prisms with striated faces. It has a pleasant acid taste, gives off its water (9·41 per cent.) at 100°, dissolves in 11·3 pts. water at 19°, in a much smaller quantity of boiling water, but is insoluble in alcohol.

Sodio-ammonic and *Sodio-potassic racemates* exist only in solution, being separated by recrystallisation into mixtures of equal quantities of the corresponding dextro- and lævotartrates.

Racemate of Strontium, $C^4H^4Sr''O^6.4H^2O$.—Precipitated by racemic acid, from strontia-water in white flocks, and by the neutral potassium-salt from chloride of strontium, as a crystalline precipitate. It gives off its water (22·87 per cent.) at 100°, is nearly insoluble in cold, and only slightly soluble in boiling water; dissolves easily in hydrochloric acid, but is insoluble in acetic acid.

Racemate of Thallium forms small, closely-aggregated, easily soluble crystals, resembling those of the neutral ammonium-salt. $\infty P : \infty P = 100°$. (De la Provostaye, Ann. Ch. Pharm. cxxvi. 79.)

Racemate of Tin is very soluble and crystallisable.

Racemate of Zinc.—Racemic acid dissolves zinc with evolution of hydrogen, and the solution yields by evaporation colourless needles of racemate of zinc. Racemic acid forms with acetate of zinc, a gelatinous precipitate, nearly insoluble in water and difficult to dry.

Nitroracemic acid. $C^4H^4(NO^2)^2O^6$. (Dessaignes, J. Pharm. [3] xxxii. 46).—Prepared by quickly dissolving perfectly dehydrated and finely pulverised racemic acid in lukewarm nitric acid of specific gravity 1·52, and mixing the decanted solution with half its volume of strong sulphuric acid. The resulting magma dried between bricks under a bell-jar, forms a light white silky mass, the saturated solution of which in lukewarm water yields, when filtered and cooled to 0°, nacreous prisms, thinner and shorter than those of nitrotartaric acid. It has no action on polarised light. In aqueous solution it decomposes, giving off gas and yielding tartronic acid, together with other products. It dissolves without decomposition in absolute alcohol, and crystallises therefrom by spontaneous evaporation, in small plates composed of microscopic crystals. It forms a precipitate with basic acetate of lead, but not with acetate of potassium, calcium or lead, or nitrate of silver. The ammonium-salt decomposed by sulphydric acid, yields racemic and tartaric acid.

RACEMIC ETHERS. The only known compounds of this group are the acid racemates of ethyl and methyl.

Ethyl-racemic acid, or *Racemovinic acid*, $C^6H^{10}O^6 = C^4H^5(C^2H^5)O^6$ (Guérin-Varry, Ann. Ch. Phys. [2] lxii. 77).—Produced by boiling 4 pts. absolute alcohol with 1 pt. of racemic acid, and cohobating the mixture in a retort at a gentle heat till the liquid evaporated to a syrup no longer deposits any solid matter on cooling. It is then diluted with water, and saturated with carbonate of barium; the filtrate is evaporated at 50° or 60°; and the crystallised ethyl-racemate of barium thus obtained is decomposed by sulphuric acid.

Ethyl-racemic acid crystallises in colourless elongated prisms with obliquely inclined bases, deliquescent, very soluble in water and in alcohol, insoluble in ether. The solution has no action on polarised light, and is decomposed by ebullition into alcohol and racemic acid, which crystallises out.

Ethyl-racemic acid is decomposed by dry distillation, yielding alcohol, water, ethylic acetate, acetic acid, ethylene gas, pyroracemic acid, &c.—*Nitric acid* converts it into acetic, carbonic, and oxalic acids. Its solution dissolves *zinc* and *iron*, with evolution of hydrogen; yields with potash a pulverulent precipitate, and with soda an opaline precipitate, which appears just before the liquid becomes neutral, and increases with the quantity of acid added. When added drop by drop to *baryta-water*, it forms a precipitate, which diminishes as the liquid approaches neutrality, but reappears when the acid is added in excess. The precipitate is soluble in nitric acid.—With *lime-water* ethyl-racemic acid forms a precipitate insoluble in water, and in excess of the acid, but soluble in nitric acid. The acid does not produce any turbidity with calcic or sodic sulphate. It forms a white precipitate with *acetate of lead*, and with a concentrated solution of *nitrate of silver*.

Ethyl-racemic acid is monobasic. Its salts crystallise, but not so well as the ethyl-tartrates: some of them contain water of crystallisation, which they give off in a vacuum.—The *barium-salt*, $C^{12}H^{18}Ba''O^{12}.2H^2O$, crystallises in small prisms arranged in nodular groups. It is much more soluble in hot than in cold water, insoluble in absolute alcohol and in ether.—The *potassium-salt*, $C^6H^9HO^6.H^2O$, forms prisms, apparently monoclinic, gives off 7·56 per cent. water in vacuo.—The *silver-salt*, $C^4H^5AgO^6$, crystallises in prisms slightly soluble in cold water, decomposing at 100°.

Methyl-racemic acid, $C^5H^8O^6 = C^4H^5(CH^3)O^6$ (Guérin-Varry, *loc. cit.*)—Prepared by dissolving 1 pt. of racemic acid in 1 pt. of methylic alcohol, at the boiling heat, evaporating to a syrup at a temperature below 100°, leaving the syrup to evaporate freely, and drying the resulting crystals in a vacuum. It forms colourless rectangular prisms truncated on the longitudinal edges, and passing into rhomboïdal prisms. It dissolves easily in *water*, *alcohol*, and *wood-spirit*, slightly in ether. By boiling with water, it is resolved into methylic alcohol and racemic acid. Its aqueous solution decomposes *zinc* and *iron*, with evolution of hydrogen. With *baryta-water*, it forms a precipitate soluble in excess of the acid, and in water; with *lime-water*, it forms a precipitate composed of radiate groups of acicular prisms, insoluble in excess of the acid. Methyl-racemic acid does not precipitate caustic soda or carbonate of sodium.

Methyl-racemate of Barium, $C^{10}H^{14}Ba''O^{12}.4H^2O$, crystallises in monoclinic prisms, which give off part of their crystallisation-water on exposure to the air. When not effloresced, it softens at 60°, and at 100° gives off vapours, which condense in beautiful crystalline laminæ. It is more soluble in hot than in cold water, insoluble in alcohol and ether.—The *lead-salt* is precipitated on pouring methyl-racemic acid into a solution of lead-acetate; the precipitate redissolves in excess of acid.—The *potassium-salt*, $2C^5H^7KO^6.H^2O$, forms rectangular prisms, which are decomposed, by prolonged ebullition with water, into methylic alcohol and acid racemate of potassium. Methyl-racemic acid added to aqueous potash forms a pulverulent precipitate soluble in a large quantity of water.—The *silver-salt*, $C^5H^7AgO^6$, is precipitated on adding methyl-racemic acid to a moderately concentrated solution of silver-nitrate; it is soluble in excess of methyl-racemic acid.

RACEMOCARBONIC ACID. *Desoxalic acid*, $C^5H^6O^8 = \left.\begin{matrix}(C^5H^3O^5)'''\\H^3\end{matrix}\right\}O^3$. (Löwig, J. pr. Chem. lxxix. 455; lxxxiii. 129; lxxxiv. 1; Jahresb. 1860, p. 404; 1861, p. 601.)—This acid, which contains the elements of racemic acid and carbonic anhydride ($C^5H^6O^8 = C^4H^6O^6 + CO^2$), is produced in the form of an ethylic ether, by the action of sodium-amalgam on ethylic oxalate. It is probably formed by the deoxidation of oxalic acid, thus:

$$5C^2H^2O^4 + H^2O - O^5 = 2C^5H^6O^8;$$

whence the name *desoxalic acid;* but the reaction is complicated, yielding a number of products which have not been thoroughly investigated.

Preparation.—An amalgam of 30 grms. sodium and 800 to 2,000 grms. mercury is agitated in a glass cylinder with about an equal part of ethylic oxalate, the mass being kept cool by occasionally plunging the vessel into cold water; the resulting unctuous mass is stirred up with ether, the liquid is decanted from the mercury; the residue is treated several times more with ether; the united ethereal liquids are left at rest for a while; and the clarified solution, decanted from the sediment, is repeatedly and violently agitated with small quantities of water, till a pasty mass no longer separates from it, and the ethereal solution rises to the surface free from colour. This ethereal solution, when freed from the greater part of the ether by distillation, and left to evaporate in a warm place, deposits, after a while, large transparent shining crystals of ethylic racemocarbonate, which increase in quantity on further evaporation, while the uncrystallisable portion thickens to a yellow syrup.

The ethylic racemocarbonate may be converted by heating with carbonate of potassium, or by treatment with caustic potash, into alcohol and racemocarbonate of potassium; the solution of this salt, precipitated by nitrate of lead, yields the corresponding lead-salt; and this, when decomposed by sulphuretted hydrogen, yields racemocarbonic acid, the filtered solution of which may be made to crystallise, by first evaporating it at a gentle heat over the water-bath, and then leaving it under a bell-jar over oil of vitriol.

Properties and Reactions.—Racemocarbonic acid thus obtained is a dry crystalline mass, yielding a dazzling white powder. It is very soluble in water and in alcohol, and deliquesces in the air. It softens at the heat of the water-bath, and at a somewhat high temperature becomes dark-coloured; swells up, giving off an odour like that of burnt tartaric acid; then carbonises, and burns with a faintly luminous flame, leaving no residue. When its dilute aqueous solution is heated for some time to 100° in a sealed tube, it splits up into racemic acid and carbonic anhydride.

Racemocarbonates.—Racemocarbonic acid is tribasic, the formula of its neutral salts being $C^5H^3M^3O^8$. It likewise forms acid and basic salts.—The *neutral potassium-salt*, $C^5H^3K^3O^8$, formed by direct neutralisation, or by decomposing the ethylic ether with caustic potash, or boiling it with potassic carbonate, remains, on leaving its aqueous solution to evaporate, as a gummy mass, which becomes crystalline after standing over oil of vitriol, and dries up at 100° to a white porous mass. The solution yields the barium-, lead-, and silver-salts by double decomposition.—An *acid potassium-salt*, $C^5H^4K^2O^8$, is obtained by decomposing the ethylic ether with a solution of potash in absolute alcohol, as a viscid mass, which dries up to a dazzling white powder, becoming moist on exposure to the air. The same salt is obtained in shining white crystalline crusts, by supersaturating a solution of racemocarbonic acid in potash with acetic acid. It has a slightly sour taste, dissolves in 19·4 pts. water at 16°, and does not decompose till heated above 100°.—The *neutral sodium-salt* is very soluble, and decomposes at 130°.—The *barium-salt*, $C^{10}H^6\overset{''}{Ba}{}^3O^{16}$, and the *calcium-salt*, $C^{10}H^6\overset{''}{Ca}{}^3O^{16}.3H^2O$, are white powders. When racemocarbonic acid is mixed with excess of lime-water, and the bulky precipitate is dissolved in a few drops of hydrochloric acid, the solution instantly yields with ammonia a flocculent precipitate of calcic racemocarbonate, whereas the racemate is precipitated under similar circumstances as a heavy crystalline powder, and only after the lapse of a few seconds.—The *neutral lead-salt*, $C^{10}H^6\overset{''}{Pb}{}^3O^{16}$, is when dry, a dazzling white powder, not quite insoluble in hot water. It appears to retain 1 at. water at 100°.—A *basic lead-salt*, $C^{10}H^6\overset{''}{Pb}{}^3O^{16}.C^{10}H^4\overset{''}{Pb}{}^4O^{16}$, is obtained as a bulky precipitate, by heating the aqueous solution of the ethylic ether with basic acetate of lead.—The *neutral silver-salt*, $C^5H^3Ag^3O^8$, is a white precipitate, soon turning black when moist, slightly soluble in water, easily soluble in dilute nitric and in racemocarbonic acid, the latter solution depositing a mirror of silver on standing.—A somewhat more soluble *acid silver-salt*, $C^5H^4Ag^2O^8$, is obtained by precipitating the corresponding potassium-salt with nitrate of silver.—The precipitates formed in the solution of the neutral potassium-salt by the sulphates of *zinc*, *copper*, and *manganese*, dissolve in excess of the precipitant.

Ethylic Racemocarbonate, $C^{11}H^{18}O^8 = C^5H^3(C^2H^5)^3O^8$, prepared as above described, forms large, transparent, colourless, highly lustrous crystals, which resemble chlorate of sodium, but do not appear to belong to the regular system. They retain their lustre for months, dissolve in 10 pts. water at 16°, also in alcohol and ether, have no odour, but a strong purely bitter taste, melt at 85°, forming a liquid which solidifies again at 85°. When the fused compound is exposed for some time to the heat of boiling water, it remains after cooling as a thick oily liquid, which does not solidify for a considerable time. The ether may be sublimed by careful heating in a glass tube, but if heated for some time to 140°—150°, it yields on cooling (without loss of weight) a perfectly colourless, syrupy, extremely bitter mass, which no longer solidifies. When distilled in a retort, it leaves only a trace of carbonaceous residue; the distillate is oily, has a bitter taste, and does not appear to contain racemocarbonic acid.

Ethylic racemocarbonate heated with baryta-water, caustic alkalis, or alkaline carbonates, is decomposed, yielding alcohol and a racemocarbonate of barium, &c. (p. 40). When a dilute solution of the ether, slightly acidulated with sulphuric or hydrochloric acid, is heated to 100° in a sealed tube, the racemocarbonic acid is resolved into carbonic anhydride and racemic acid. If, on the other hand, a concentrated solution of the ether is used, only partial decomposition takes place; and Löwig thinks it probable that an acid intermediate between racemocarbonic and racemic acid, or perhaps a compound of the two, may be formed. When a dilute solution of ethylic racemocarbonate containing a little sulphuric or hydrochloric acid, is boiled in a platinum dish, scarcely any gas is evolved, so long as the water lost by evaporation is renewed; but on subsequently concentrating the liquid, it becomes darker and gives off gas. The syrupy liquid remaining, after the hydrochloric acid has been completely expelled, solidifies on cooling to a brittle friable mass, easily soluble in water; and if the concentrated solution be left to evaporate, a tolerably abundant crystallisation of racemic acid is obtained; the greater part, however, forms a syrupy acid, which dries up over oil of vitriol to a translucent mass, and yields a silver-salt having the composition of silver-racemate.

The yellow syrup (p. 40), obtained together with the crystals in the preparation of ethylic racemocarbonate, is an uncrystallisable modification of that compound. By heating it with strong hydrochloric acid, and then evaporating off the whole of that acid, a very acid syrup is obtained, which dries up over oil of vitriol to an amorphous transparent mass, easily soluble in water. The acid thus obtained is isomeric with racemic acid, but is distingushed from that acid and from racemocarbonic acid by its reaction with lime-water, yielding therewith a precipitate, which when dissolved in a small quantity of hydrochloric acid is not reprecipitated by ammonia. Moreover, it does not form a sparingly soluble acid salt with potash. (Löwig.)

RADIATION AND CONDUCTION OF HEAT. There are various modes in which heat may be transferred from one place to another. Of all these, the most easily intelligible—in the sense of our being able clearly to conceive and follow the several parts of the process—consists in the bodily movement of heated matter. A very important case of the transference of heat in this manner is presented by the so-called phenomena of *convection*, upon which the distribution of heat in liquid and aëriform bodies almost entirely depends. Another way in which the motion of material bodies may intervene, as the medium of the transference of heat, is exhibited in many cases of the evolution of heat by mechanical means. For instance, if a steam-engine is employed to overcome friction, or to do other work in opposition to molecular forces, and so to develop heat, the process may be correctly described, so far as the general result is concerned, as consisting in the transfer of part of the heat of combustion of the coals, from the furnace to the place where the heat-producing work is performed. In other cases, again, electricity is the medium of the transference of heat from one place to another. But, in addition to all these various ways in which the motion of heat may be brought about by the action of other forms of energy, there are two distinct ways in which it can occur without the intervention of energy in any other form. These are RADIATION, or the spontaneous outflow of heat in all directions which is constantly taking place at the free surface of material bodies; and CONDUCTION, or the propagation of heat by communication through the substance of material bodies, whereby the temperature of every mass of matter tends constantly to become uniform throughout. We shall attempt in this article to state the most important laws and conditions by which the transference of heat in these two ways has been found to be determined.

RADIATION.

The radiation of heat is a phenomenon completely analogous to the radiation of light; in fact, all the known properties of radiant heat and of light point to the conclusion, that there is no difference of a fundamental kind between them. And if, as seems inevitable, we adopt the hypothesis that temperature in material bodies consists in a vibratory or other movement of their particles (HEAT, iii. 131), we must regard radiation, whether of heat or light, as due to vibrations of the luminiferous ether (LIGHT, iii. 589), excited by the heat-vibrations of the particles of ordinary matter, and propagated by the ether in all directions from their source. According to this view, a radiating body may be compared with a vibrating tuning-fork, or other source of sound; and the rays of heat or light which it emits, with the progressive undulations, constituting waves of sound, which the vibrations of the sounding body excite in the air. The cooling of a heated body by radiation would thus answer to the gradual dying-out of the vibrations of the tuning-fork, as it gives up its motion to the air: any circumstance which increases the rate of radiation, that is to say, the quantity of heat given out in a given time, hastening the fall of temperature of the heated body; just as whatever increases the amount of motion imparted to the air in a given time by a vibrating fork, and so augments the loudness of the resulting sound, causes the fork to come to rest more quickly. On the same view, a rise of temperature in a material body, caused by rays of heat absorbed by it, would correspond with the production of sympathetic vibrations in solid bodies under the influence of sound-waves transmitted to them through the air; and just as those conditions, which facilitate most the communication of motion by a vibrating body to the air, are also the conditions most favourable to its being thrown into vibration by undulations of the air, so, as we shall see, the conditions which most promote the loss of heat by radiation are also those which are most favourable to the absorption or gain of heat in the same way. Again, the different refrangibility which characterises rays of light of various colours, as well as rays of heat from various sources, being caused by different rates of vibration, corresponds to the different pitch of various sounds. (On the analogies of heat and sound, comp. Thomas Young, *Lectures on Natural Philosophy*, 2 vols. 4to. Lond. 1807, vol. i. p. 656.)

Radiation, considered as a mode of transference of heat, is obviously a process which can only go on between at least two material bodies, of which one gives out, and the other receives, heat. And, except in the case of radiation through a vacuum, a third body also intervenes in the phenomenon—namely, that *through* which the radiation takes place. Hence the entire process consists of three distinct parts—Emission, Absorption, Transmission—the course of each of which is dependent on the physical properties of the particular material substances concerned. But, before considering radiant heat in relation to the properties of individual substances, we will briefly describe its general properties, and enumerate the most important and decisive of the experiments by which the essential identity of radiant heat and light has been proved, and which therefore justify the conclusion that radiant heat, like light, consists in undulations propagated by the luminiferous ether, in the same way as waves of sound are propagated by the air.

1. *Radiant heat traverses a vacuum, or any homogeneous medium, in straight lines.*

This fact is proved, like the corresponding fact in the case of light, by the effect of opaque screens, which, with the exceptions mentioned at page 46 (parag. 7), prevent the heat of any radiant source from arriving at any point so situated that a straight line drawn from it to the source would cut such a screen.

2. *Radiant heat is emitted in straight lines in all directions from a radiating point.* Hence the quantity of heat which in a given time falls on a given surface from a radiating point is *inversely proportional to the square of the distance* of that surface from the radiating point. The most complete and decisive proof of this law was furnished by Melloni, who showed that when a thermo-electric pile (ELECTRICITY, ii. 413; HEAT, iii. 22), fitted with a non-reflecting cone, is turned towards a large, flat, uniformly heated surface, the heating effect, as shown by the deflection of the needle of a galvanometer connected with the pile, is the same at all distances of the pile from the heated surface. In this case the portion of the flat surface subtended by the face of the pile, or *visible* therefrom, *increases* proportionably to the square of the distance: that is to say, the number of points of the heated surface from which rays can reach the pile is *directly proportional* to the square of the distance; but, since the total heating effect remains the same at all distances, it follows that the effect of each point must be *inversely proportional* to the square of its distance from the pile. (Melloni, *La Thermochrôse*, Naples, 1850, p. 129.)

3. The *velocity of propagation* of radiant heat has not yet been measured directly, in consequence of the time required by it to produce sensible effects being greater than the time of its transmission through such distances as are available for experiment. There is, however, every reason to suppose that, in substances not possessed of dispersive power, it is the same as that of light. Melloni found the time of transmission through 357 feet of air inappreciably short. (*Op. cit.* pp. 121–123.)

4. It follows, from the laws which hold with respect to the propagation of wave-motions, that, whenever a train of waves arrives at a surface, on opposite sides of which the relation between the elasticity and density of the medium of propagation is different, *partial* or *total reflection* must take place; and that this reflection must take place so that the reflected ray lies in the same plane with the incident ray, and the normal to the reflecting surface at the point of incidence, and that the incident and reflected rays make equal angles with the normal. That radiant heat is thus *reflected* on arriving at the surface of separation of two media, may be proved by means of a thermo-multiplier placed in such a position relatively to a source of heat and a plane metallic reflector, that the radiation from the source cannot reach it, except by the rays being reflected in accordance with the above conditions. The equality of the angles of incidence and reflection can be still more decisively demonstrated by means of two parabolic reflectors placed with their concave surfaces towards each other, and their axes coincident: if a source of heat be placed in the focus of one reflector, the rays which strike this reflector will be brought to a focus again at the focus of the other reflector.

But, as in the case of light, this law can only be recognised when reflection takes place at polished surfaces, that is, at surfaces each element of which is situated sensibly at the same plane, or coincides with the same curve. Since, however, even with the most perfect polish that can be obtained, many superficial elements are doubtless inclined in directions which do not coincide with the general form of the surface, the intensity of the heat reflected in such a direction as to make with the normal to the general surface an angle equal to that made by the direction of the incident heat, is always less than the intensity of the incident heat, even allowing for the quantity which may penetrate the reflecting surface. The amount of heat thus irregularly reflected, or *diffused*, necessarily varies with the nature of the reflecting surface, being less, under otherwise similar circumstances, in proportion as the latter is more perfectly polished; it also varies with the absolute value of the angle of incidence.

The fact of the diffusive reflection of heat was first placed beyond doubt by Melloni, whose method of experiment consisted in determining, by means of the thermo-multiplier, the relative quantities of heat radiated obliquely by very thin unpolished screens, upon which rays were incident normally from a source of heat. The screens were so thin that both surfaces might be regarded as having the same temperature; nevertheless, the quantity of heat radiated in a direction making a given oblique angle with the surface turned towards the source of heat, exceeded that radiated in a direction making the same angle with the other surface; showing that the radiation from the former surface did not consist entirely of the heat given out by the screen itself, but also, in part, of heat irregularly reflected. The influence of the absolute value of the angle of incidence on the proportion of heat reflected irregularly, has been investigated by Knoblauch. With solar heat and, in one set of experiments, a glass mirror blackened at the back, and in another set with a metallic mirror, he obtained the following results:—

Angle of Incidence measured from the Mirror.	Deflection of the Galvanometer-needle produced by the Rays regularly reflected—	
	From the Blackened Mirror.	From the Metallic Mirror.
60°	10·0°	56·0°
50	10·0	55·0
40	11·0	54·5
30	15·1	53·0
20	28·1	48·0
10	43·0	43·0

The numbers in the last column show that the quantity of heat reflected regularly by the metallic mirror diminished, and consequently the quantity reflected irregularly increased, as the incident rays made a smaller angle with the surface of the mirror. The increased reflection from the glass mirror at low angles of incidence is to be attributed, not to diminished diffusion, but to diminished absorption.

4. In addition to the portion which is reflected, regularly or irregularly, when radiant heat arrives at the surface of separation of two media, a certain quantity usually—perhaps always—penetrates the second medium. Of the heat which thus passes onwards into the second medium, a greater or less proportion is always *absorbed;* or, in the language of the view we have adopted respecting the nature of radiant heat, the vibratory motion of the particles of the ether is given up to the material particles of the medium. The proportion of heat so absorbed varies, from a barely perceptible amount, even when a considerable thickness of the second medium is traversed, as in the case of rock-salt, to the total quantity which enters the medium, as in the case of the metals, in which the absorption of heat is so complete, within a very short distance from the surface, that it was only by employing exceedingly thin films of metal, deposited on glass by chemical means, that Knoblauch succeeded in proving that the metals are not absolutely impenetrable by radiant heat. The proportion of radiant heat absorbed in its passage through a given thickness of a given medium is not, however, a constant quantity; it varies to a great extent, as we shall presently see, with the temperature of the source from which the heat comes, just as the absorption of light by various media depends on the colour of the light.

5. Another consequence of the general principles of wave-motion, is that, upon the theory we have adopted, when radiant heat passes from one medium into another, in which the elasticity and density of the luminiferous ether are to each other in a different ratio from what they were in the first medium, its velocity of propagation must be different in the two media. Consequently, if the rays of heat are incident upon the separating surface of the media in any other direction than that of the normal to the surface at the point of incidence, their direction will be altered on passing from the first medium into the second, or they will undergo *refraction;* and this refraction will take place according to the same laws as the refraction of light—that is, the refracted ray will be in the same plane with the incident ray and the normal to the surface, and the sine of the angle which the incident ray makes with the normal will be to the sine of the angle which the refracted ray makes with the normal, as the velocity of the ray in the first medium is to its velocity of propagation in the second medium (see Light, iii. 608, 609). A familiar example of the refraction of heat is afforded by the effects of burning-glasses.

The second part of the law of refraction of heat, as above stated, has not hitherto received direct experimental confirmation, for, as has been already said (p. 43), the velocity of propagation of radiant heat has not yet been measured. It is, however, abundantly proved that the *index of refraction* (Light, *loc. cit.*), corresponding to the passage of radiant heat from a given medium into a given second medium, has a constant value. But, just as there are various kinds of light, differing from each other in refrangibility (Light, iii. 618), so there are various kinds of radiant heat which differ from each other in the same way. The indices of refraction of heat of several kinds, corresponding to its passage from air into rock-salt, have been measured by Forbes, by Wollaston's method (iii. 614), depending on the total reflection which takes place when rays traversing one medium are incident very obliquely on the surface of another medium of less refractive power. In the following table (taken from Wüllner's *Lehrbuch der Experimental-physik*, 2 vols. Leipzig, 1863-65, vol. ii. p. 327) the numbers in the last column represent the indices of refraction of the rays present in greatest abundance in the heat of the various kinds specified; but it is to be understood that each kind of heat examined contained, in a smaller proportion, rays of both greater and less refrangibility than those which formed the largest part.

Indices of Refraction of Heat-rays in Rock-salt.

Kind of heat.	Index of Refraction.
Heat from a Locatelli's lamp (an oil-lamp with solid square wick but no chimney)	1·531
The same after passing through a plate of alum	1·558
" " window-glass	1·547
" " black glass	1·553
" " black mica	1·543
Heat from incandescent platinum	1·532
The same after passing through a plate of window-glass	1·548
" " black mica	1·544
Heat from brass at 371° C.	1·528
Luminous rays of mean refrangibility from the lamp	1·552

The index of refraction for crown-glass of the least refrangible solar rays has been deduced by J. Müller, from an examination of the solar spectrum produced by a prism of crown-glass, by means of a linear thermo-electric pile (Müller's *Lehrbuch der Physik*, 6th ed., ii. 743–745). Müller gives the number 1·506, but from a criticism of his experiments by F. Eisenlohr (Pogg. Ann. cix. 240), it appears that 1·516 would be more correct.

We shall have occasion, as we proceed, to return several times to the differences between the kinds of heat emitted by various sources; but we may take this first occasion, upon which such differences call for special mention, to state wherein they probably consist, and also how far there is any real difference between radiant heat and light.

If radiant heat be regarded as consisting in an undulatory motion of the luminiferous ether, all the differences (irrespective of intensity and state of polarisation) which have been observed between various rays of heat may be referred to differences in the rapidity of the vibrations by which they are produced, and consequent differences in the length of the waves of which they consist; the most refrangible rays having the most rapid vibrations and the smallest wave-length, and the least refrangible rays having the slowest vibrations and the greatest wave-length. These, it will be seen, are differences of precisely the same kind as those existing between rays of light of various colours. Hence, unless the vibrations constituting radiant heat have a different direction, or a different form, from those constituting light (of which, however, there is not the slightest evidence, for, as we shall see, *all* the characteristic properties of light, with the single exception of visibility, are shared by radiant heat), we are forced to admit that rays of heat and rays of light of the same wave-length are in all respects identical, and this conclusion is borne out by every test which it has hitherto been possible to apply (comp. iii. 632). But although there is absolutely no known difference between rays of heat and rays of light of the *same* refrangibility (rate of vibration, wave-length), rays of heat exist whose refrangibility is less, and accordingly their rate of vibration slower and wave-length greater, than that of the least refrangible rays of light. The relation between radiant heat and light may therefore be summed up as follows: All luminous rays are rays of heat, but all rays of heat are not luminous; they only become so when their rate of vibration exceeds a certain minimum limit (about 400 millions of millions per second), and their wave-length consequently falls below a certain maximum (about 7 ten-millionths of a millimetre). According to this view, the difference between radiant heat and light is subjective and not objective, being dependent on the structure of our eyes, and not upon any want of similarity between radiant heat and light themselves.

6. Like rays of light, rays of heat *interfere* with and neutralise each other, when two rays from the same source arrive at the same point by paths of very slightly different lengths. This phenomenon was first observed by Fizeau and Foucault (Compt. rend. xxv. 447), by means of Fresnel's interference-mirrors (iii. 599), and a spirit thermometer whose bulb was not more than 1·1 mm. in diameter, and which could be read to $\frac{1}{400}$th of a degree centigrade. When this instrument was gradually moved across the middle of the field, the readings were successively, 20·9, 35·9, *and* 20, the number 35·9 corresponding to the middle of the central fringe.

Knoblauch afterwards (Ann. Ch. Phys. [3] lix. 493) observed the same phenomenon by means of a Pouillet's interference-prism (iii. 600), and a linear thermo-electric pile; and the same philosopher showed, at the same time, that the positions of the alternate maxima and minima of heating effect (corresponding to the light and dark bands in the case of light) suffered a lateral displacement when a slightly wedge-shaped piece of glass was interposed between the prism and the thermo-electric pile, thus proving that the velocity of propagation of radiant heat is not the same in glass as it is in air. (See LIGHT, iii. 601.)

Knoblauch has likewise demonstrated the interference of radiant heat under the same circumstances as those under which the colours of thin plates (iii. 643) are produced by light.

7. *Diffraction* (iii. 601) of radiant heat occurs when rays from a source of sufficiently small extent pass through a small aperture, or by the edge of an opaque screen. Knoblauch ascertained that when heat from a linear source passes through a narrow slit, the thermal effect on the farther side of the slit extends to points which the rays could not reach if they all followed straight paths; and he found that the lateral extension of the heating effect increased (1) with the distance from the slit of the position where the effect was examined, (2) with the narrowness of the slit, and (3) with the distance of the slit from the source of heat.

The diffraction of radiant heat and the simultaneous interference, when it passes the edge of a simple screen, were observed by Fizeau and Foucault; and its diffraction by "gratings" (iii. 605), by Seebeck in 1849 (Pogg. Ann. lxxvii. 574), and subsequently by Knoblauch.

8. The interference and diffraction of radiant heat prove conclusively that it consists in undulations; and that these undulations, like those of light, take place in directions perpendicular to that in which the undulatory movement advances, is proved by the phenomena of the *polarisation* of radiant heat. Like light, radiant heat may be polarised, by reflection, by ordinary refraction, by double refraction, and by absorption in doubly-refracting crystals.

The polarisation of heat by reflection from the surface of glass was distinctly proved in 1812 by Bérard, who showed that when heat was reflected successively by two glass mirrors, the intensity of the beam reflected from the second mirror was decidedly greater when the plane of reflection of the two mirrors coincided, than when they were at right angles to each other. But the accurate investigation of the phenomena of the polarisation of heat is chiefly due to Knoblauch and De la Provostaye and Desains (Ann. Ch. Phys. [3] xxvii. 109; xxx. 159; 267; 276). Knoblauch found that, as in the case of light so in that of radiant heat, the polarisation produced by reflection is most complete when the rays are incident at some particular angle depending on the nature of the reflecting substance. Thus, out of 100 rays reflected from glass at various angles (measured from the normal), he found the proportion of polarised rays to be that stated below:—

Angle of Incidence	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.	75°.	80°.
Percentage of polarised heat in the whole quantity reflected	0·0	11·1	40·6	66·6	66·6	69·2	69·2	74·1	44·4	30·5	28·4	25·0	18·8

It will be seen that the maximum of polarisation occurred when the angle of incidence was 55°, which agrees almost exactly with the angle (54° 35′) at which the most complete polarisation takes place in the case of luminous rays (iii. 653). When a steel mirror was used as the polarising apparatus, the maximum of polarisation (34 per cent. of the total heat reflected) occurred with an angle of incidence of about 75°.

De la Provostaye and Desains not only proved that the polarisation of heat takes place under the same conditions as the polarisation of light, but showed that the properties of polarised heat agree precisely with those of polarised light. Fresnel had established that, when polarised light is reflected at the surface of a transparent medium, the intensity of the reflected light may be expressed by the formula $\frac{\sin^2(i-r)}{\sin^2(i+r)}$ when the plane of polarisation is parallel to the plane of reflection, and by the formula $\frac{\tan^2(i-r)}{\tan^2(i+r)}$ when the plane of polarisation is perpendicular to the plane of reflection, i and r denoting the angles of incidence and refraction respectively. Taking the index of refraction of glass as $= 1{\cdot}52$, De la Provostaye and Desains calculated the intensity of the reflected beam for various angles of incidence, for the two cases to which these formulæ correspond, and found the results to agree precisely with those furnished by direct experiments with polarised heat, as shown by the following table:—

Reflection of Polarised Heat.

Heat polarised in plane of incidence.			Heat polarised at right angles to plane of incidence.		
Angle of incidence.	Intensity of reflected beam.		Angle of incidence.	Intensity of reflected beam.	
	Observed.	Calculated.		Observed.	Calculated.
80	55·1	54·6	80°	24·0	23·6
75	40·7	40·8	75	11·0	10·6
70	30·6	30·8	70	4·3	4·15
60	18·0	18·3	28	3·0	2·9
50	11·7	11·7			
40	8·1	8·1			
30	6·1	6·1			
20	5·0	5·0			

De la Provostaye and Desains have likewise observed that rotation of the plane polarisation of heat is caused when polarised heat is transmitted through a piece of heavy glass placed between the poles of a powerful electro-magnet, and also when it is made to pass through certain liquids, such as oil of turpentine and solution of sugar, and have ascertained that in both cases the action is precisely the same as in the analogous phenomena presented by polarised light (see iii. 671 and 676). Some of the numerous other points of agreement which the same observers have detected between the properties of polarised heat and polarised light, are mentioned below in connection with the double refraction of heat.

The polarisation of heat by ordinary refraction was observed by Forbes (Phil. Mag. [3] vi. 209) and Melloni, but this phenomenon also has been more completely investigated by Knoblauch and De la Provostaye and Desains, than by previous observers. It has been shown by their experiments, that when a beam of radiant heat is incident upon a bundle of thin plates of glass at the polarising angle, it is separated into two parts—a reflected beam polarised in the plane of incidence, and a refracted beam polarised at right angles to the plane of incidence; and they have also proved that the intensity with which a beam of polarised light is transmitted through one or more plates of glass can be calculated by precisely the same formulæ as those which apply in the case of light.

9. The same investigators have demonstrated the *double refraction* of heat, and proved that the phenomenon agrees in all respects with the double refraction of light. Knoblauch caused a pencil of solar rays, reflected from a heliostat, to fall upon the natural-cleavage faces of a crystal of calc-spar, and received the transmitted rays upon a thermo-electric pile, the face of which presented only a vertical strip of 0·25 mm. in width. As the pile was placed successively in the path of one of the luminous beams produced by the double refraction of the incident light, in the dark space between the two beams, and in the path of the second luminous beam, the needle of the galvanometer was deflected to 20·5°, then came back to 5°, and was then deflected again to 20·75°, showing that the heat-rays had been completely separated into two pencils of equal intensity. Knoblauch further found that, when the crystal was turned round the incident ray as an axis, one of the transmitted pencils of heat-rays (the extraordinary pencil) rotated round the other (the ordinary pencil), which remained stationary.

Similar results have been obtained by De la Provostaye and Desains. A beam of solar rays was directed, by means of a heliostat, on to an achromatic double-image prism, and, one of the emergent beams being stopped by a screen, the other was received upon a glass mirror placed vertically, whereby it was reflected at an angle of 56° upon the the thermo-electric pile. When the principal section of the prism was horizontal, and the ordinary ray (which was consequently polarised in a horizontal plane, iii. 654) was allowed to fall upon the mirror, the galvanometer-needle was deflected to 75°, whereas it remained completely at rest when the prism was turned round through 90°; thus proving that the two transmitted beams were completely polarised in planes at right angles to each other, a result which was also arrived at by Knoblauch.

De la Provostaye and Desains have also proved that when a beam of polarised heat falls upon a doubly-refracting crystal, so that the plane of polarisation is neither parallel with, nor perpendicular to, the principal section of the crystal, it is broken up into two beams whose relative intensities follow the same law as the intensities of the two beams of light produced under similar circumstances. In the case of light, if the intensity of the incident beam be represented by I, that of the ordinary refracted beam by O, that of the extraordinary refracted beam by E, and the angle which the plane of polarisation makes with the principal section of the crystal by α, **Malus** showed that these quantities are related to each other as follows:—

$$O = I \, . \cos^2\alpha; \qquad E = I \, . \sin^2\alpha.$$

Putting I = 1, De la Provostaye and Desains found the following values for O corresponding to various values of α: namely, for—

$$\begin{array}{ccccccccc} \alpha & = & 30^\circ, & = & 35^\circ, & = & 45^\circ, & = & 52^\circ \\ O & = & 0{\cdot}75, & = & 0{\cdot}67, & = & 0{\cdot}50, & = & 0{\cdot}3 \end{array}$$

results which agree exactly with the above formula.

When a doubly-refracting crystal absorbs one of the two beams produced by double refraction, as is the case to a great extent with tourmaline cut parallel to the principal axis (iii. 655), the beam which is transmitted is necessarily polarised, either in the case of light or heat. The polarisation of heat by tourmaline, observed by **Forbes**, was the earliest discovered instance of the polarisation of heat by double refraction; and it was supposed by him for a time to reveal an essential difference between radiant heat and light, since he found the polarisation of heat from some sources apparently much less complete than that of light. The cause of this apparent anomaly was afterwards ascertained by Melloni to be that, although tourmaline is opaque for luminous rays whose vibrations take place perpendicularly to its principal axis, and therefore completely absorbs one of the two luminous beams, it is not equally opaque for rays whose vibrations are perpendicular to the axis but are as slow as those of the invisible heat-rays.

Having thus briefly stated the most important of the general properties of radiant heat, we have still to consider it in its relation to material bodies, under the three heads of Emission, Absorption, and Transmission.

Emission of Radiant Heat.

It is a matter of universal experience, that, under otherwise similar circumstances, a given body gives out more heat in a given time, the hotter it is. Temperature, therefore, is one condition which determines the emissive power of bodies for heat; but further examination shows that it is not the only condition upon which this phenomenon depends. It was observed as early as 1804, by **Leslie**, that different substances have very different powers of emitting heat, even when their temperatures are exactly the same. He placed in front of a concave metallic mirror a cubical metal vessel filled with boiling water, and put one bulb of a differential thermometer in the focus of the mirror, the other bulb being protected from the radiation. By coating the different sides of the cube with the various substances to be examined, and turning them successively towards the mirror, he was able to compare, by the effect on the thermometer, the relative emissive powers of the several substances, independently of any difference of temperature. **Melloni** subsequently made similar comparative experiments, using his thermo-multiplier instead of Leslie's differential thermometer. Among all the substances examined, both Leslie and Melloni found that lampblack had the greatest emissive power, or at least that the emissive power of no other substance exceeded it, and they accordingly adopted it as a standard of comparison for all the rest. The numerical results given in the following table are, therefore, to be understood as giving the intensity of the radiation at 100° C. from a superficial unit of each of the substances named, the radiation from a unit of surface covered with lampblack being taken at 100:—

Emissive Powers for Radiant Heat at 100° C.

Leslie.				Melloni.	
Lampblack	100	Mica	80	Lampblack	100
Paper	98	Graphite	75	White lead	100
Resin	96	Tarnished Lead	45	Isinglass	91
Sealing-wax	95	Mercury	20	Indian ink	85
Crown-glass	90	Polished Lead	19	Gum-lac	72
Indian ink	88	Polished Iron	15	Polished Metals	12
Ice	85	Tinplate	12		
Red lead	80	Gold, Silver, Copper,	12		

The exact numbers in this table cannot, however, lay claim to any very great degree of accuracy. For it was found both by Leslie and Melloni, that the radiating power of the same substance varied considerably according to the condition of its surface, and the same fact has been repeatedly observed by later investigators. The metals, for instance, when polished, radiate much less than they do when tarnished or roughened. That a tarnished metallic surface should have a different emissive power from a bright metal is not surprising: for the tarnish consists in the formation of a thin film of oxide or sulphide, and it is this film, and not the metal itself, which forms the true surface from which a great part of the radiation proceeds. But even when the chemical nature of the surface undergoes no change, the emissive power is often affected to a considerable extent by the physical state of the surface. This is very distinctly shown in the following experiment of Melloni's (*Thermochrôse*, p. 87, note): he prepared four plates of pure silver, two of which were strongly hammered, and the other two simply cast and not hammered; all four plates were then polished with pumice-stone and charcoal, but without the use of a hammer or burnisher; and lastly, one plate of each pair was scratched by rubbing it in one direction with coarse sandpaper. The four plates so prepared were used to form the vertical sides of a cube which was filled with boiling water, and the radiating power of the four sides was determined. The deflections of the galvanometer-needle which they severally produced were—

	Polished.	*Scratched.*
Hammered plate . . .	10°	18°
Unhammered plate . .	13·7	11·3

The following numbers, obtained by De la Provostaye and Desains (Ann. Ch. Phys. [3] xxii. 372) for the relative radiating powers at 120° C., of several metals in different conditions, compared with the radiating power of lampblack at the same temperature taken as 100, show similar differences, although the absolute values of the numbers are considerably below those found by Melloni and Leslie. The comparisons with lampblack were made in two ways: the first method depended on determining the size of the surface of the substance under examination which caused as great a deflection of the galvanometer as a given surface of lampblack at the same temperature; in the second method the radiating surfaces were equal, and their respective radiating powers were calculated from the excess of temperature of the metals over the lampblack at which they emitted equal quantities of heat.

Emissive powers of Metals at 120° C.

	Emissive power.	
	By first method.	By second method.
Pure silver, rolled, ...	3·0	2·9
„ „ polished.	2·5	2·2
„ „ „ after long heating	2·75	3·0
Silver chemically deposited on silver	. .	2·05
Silver chemically deposited and burnished	2·25	2·2
Silver chemically deposited on copper, dull	5·4	5·3
Platinum, rolled	10·8	10·4
Platinum, polished	9·5	9·0
Gold-leaf	4·3	4·3
Copper-foil	4·9	

The general rule which may be deduced from these and numerous allied observations, is that the denser and more compact the surface of a body is, the smaller is its emissive power, while any treatment which diminishes the density of the surface increases the emissive power. The mere fact of the surface being polished or not polished, if these differences do not involve differences of density, does not affect the emissive power of a substance: thus marble, ivory, agate, quartz, selenite, and other similar substances which are capable of receiving a polish, but in which the polishing process does not alter the density of the superficial stratum, have the same emissive powers whether polished or unpolished. (Melloni, *La Thermochrôse*, p. 83, note.—Compare also Knoblauch, Pogg. Ann. lxx. 343.)

The following table gives the relative emissive power, at 100° C., of several substances in a state of fine powder, according to Tyndall's experiments:—

Emissive powers of Powders at 100° C.

Rock-salt	35·3	Sulphate of calcium	77·7
Mercuric iodide	39·7	Ferric oxide	78·4
Sulphur	40·6	Zinc hydrate	80·4
Chloride of lead	55·4	Ferroso-ferric oxide	81·3
Carbonate of calcium	70·2	Ferrous sulphide	81·7
Red lead	74·2	Lampblack	84·0
Oxide of cobalt	76·7		

Previous experimenters, in particular Masson and Courtépée (Compt. rend. xxv. 936), had concluded that the emissive powers of all substances, in a sufficiently fine state of division, were equal; but, according to Tyndall, this apparent result was due to the powders examined having been mixed with gum in order to attach them to a metallic surface, whereby radiation from the gum took the place, to a great extent, of radiation from the particles of powder enveloped by it.

Another circumstance which exerts an influence on the quantity of heat emitted by a given substance at a given temperature, is the *thickness* of the radiating stratum. The effect of variations of this condition is not however sensible, except in the case of substances which are perceptibly transparent for radiant heat, and therefore allow the particles which lie below the actual surface to take part in the radiation, such as glass and varnishes of various kinds; with metals, on the other hand, which are completely opaque for radiant heat as well as for light in any thickness in which they can be used, the effect of variations of thickness is imperceptible. Thus Melloni found, on applying successive coats of varnish to the metal face of a radiating cube, that the radiating power was increased by each coat of varnish up to the sixteenth; but on coating one of the faces of the cube with gold-leaf of various thicknesses, the radiating power was diminished to the same extent in each case

The intensity of the radiation from a plane surface is not the same in all directions, but is greatest in the direction of the normal to the surface. Leslie, who investigated this point experimentally, believed that the radiation in any direction was proportional to the cosine of the angle which that direction made with the normal; that is to say, if R represents the quantity of heat radiated by a unit of surface in the direction of the normal to the surface, and R′ the quantity of heat radiated by a unit of surface in any direction making an angle α with the normal, Leslie concluded that the relation between these two quantities might be expressed in all cases by the equation

$$R' = R \, . \cos \alpha$$

According to the experiments of De la Provostaye and Desains, however, this relation does not hold good except for a small number of substances, lampblack being one of them. They placed, between a radiating surface of considerable extent and the thermo-electric pile, a screen pierced with a comparatively small aperture, through which alone the rays could reach the pile. Now it is obvious that with this arrangement, the extent of surface from which rays could arrive at the pile was less when the surface was placed so as to radiate normally through the aperture, than when it was placed so as to radiate obliquely, and that the extent of surface from which rays were received by the pile in the latter case, was to the extent of surface from which they were received in the former case, inversely as the cosine of the angle through which the radiating body had been turned. Hence, if the intensity of the radiation from a unit of surface, varied directly as the cosine of the same angle, the total heating effect upon the pile must have remained the same for all positions of the radiating surface; this, however, was not the case except with lampblack, as will be seen from the following table:—

Emissive Powers at various Angles.

Angle of emission. (measured from normal).	Lampblack.	Glass.	White-lead varnish.	Red ochre varnish.	Black varnish.
0°	100	90·0	100	100	100
60°	. .	83·6	94·6		
70°	100	75·0	83·9	91·2	
75°	. .	65·3			
80°	100	54·4	65·9	82·3	76

From these results it appears that the emissive powers of the substances mentioned, for oblique directions, diminish more rapidly than the cosine of the angle of obliquity, except in the case of lampblack.

In considering the *effect of the temperature* of the radiating body on the quantity of heat emitted, it is important to bear in mind that what is measured in the various methods for determining the emissive powers of different bodies, is not the actual quantity of heat given out in a given time by a given extent of surface, but merely the rate of exchange of heat between the radiating body and surrounding objects, including the thermometric apparatus itself. If in a given time a thermo-electric pile gives out to a body placed opposite to it exactly as much heat as it receives back again from that body, its temperature is not altered, and the state of things is the same as though neither the pile nor the radiating body near it had any emissive power whatever. But this stationary condition will be disturbed equally by raising the temperature of the radiating body, so as to make it give out more heat than it receives in return, or by lowering the temperature of the thermo-electric pile, so as to make it give out less heat than it receives; that is to say, the same thermometric effect may be produced upon the thermo-electric pile by lowering its temperature, as by raising that of the radiating body. There is therefore obviously no reason to expect that any simple relation would be apparent between the emissive power of a given body, as measured by the methods above described, and its absolute temperature (HEAT, iii. 52), much less between this property and the temperature of the body on the centigrade or any other arbitrary thermometric scale. We might, however, expect to find the actual quantity of heat which a given body loses in a given time, proportional to the excess of its temperature over that of surrounding bodies.

To ascertain whether this is so, it is needful to examine the rate at which the same body cools in a vacuum, when its initial temperature exceeds that of the surrounding space by different known amounts. A very elaborate investigation of this subject was made by Dulong and Petit (Ann. Ch. Phys. [2] vii. 225, 337). They determined the rate of cooling of a large mercurial thermometer, placed in the middle of an exhausted brass globe kept at a constant known temperature, with various definite differences of temperature between the thermometer and the globe, and at various absolute temperatures of each. Their most important results are given in the following table, where the columns headed "Rate of Cooling" give the number of degrees through which the temperature of the thermometer would sink in *one minute* under the various conditions specified, if it continued during the whole time to lose heat as fast as at the beginning of the interval:—

Excess of temperature of thermometer over globe.	Temp. of globe = 0°. Rate of Cooling = v.	$\frac{v_1}{v}$	Temp. of globe = 20°. Rate of Cooling = v_1.	$\frac{v_2}{v_1}$	Temp. of globe = 40°. Rate of Cooling = v_2.	$\frac{v_3}{v_2}$	Temp. of globe = 60°. Rate of Cooling = v_3.	$\frac{v_4}{v_3}$	Temp. of globe = 80°. Rate of Cooling = v_4.
240° C.	10·69	1·16	12·40	1·16	14·35				
220 "	8·81	1·18	10·41	1·15	11·98				
200 "	7·40	1·16	8·58	1·16	10·01	1·15	11·64	1·15	13·45
180 "	6·10	1·15	7·04	1·16	8·20	1·16	9·55	1·15	11·05
160 "	4·89	1·16	5·67	1·17	6·61	1·16	7·68	1·16	8·95
140 "	3·88	1·17	4·57	1·16	5·32	1·15	6·14	1·17	7·19
120 "	3·02	1·17	3·56	1·17	4·15	1·17	4·84	1·16	5·64
100 "	2·30	1·18	2·74	1·15	3·16	1·16	3·68	1·17	4·29
80 "	1·74	1·15	1·99	1·16	2·30	1·18	2·73	1·17	3·18
60 "	. .	. .	1·40	1·16	1·62	1·16	1·88	1·15	2·17

From this table it appears that the rate of cooling, or quantity of heat lost in a given time, depends not merely upon the difference of temperature between the cooling body and surrounding objects, but also upon its absolute temperature. Thus, for instance, when the temperature of the thermometer was 200°, and that of the globe 0°, the rate of cooling was 7·4; but, when the temperature of the globe was 60°, and that of the thermometer 260°, the rate of cooling was 11·64, although the *difference* of temperature was the same as in the former case, namely 200°. It further appears that the quotient obtained by dividing the rate of cooling corresponding to a given excess of temperature of the thermometer, by the rate of cooling corresponding to the same excess when the temperatures of both thermometer and globe are 20° lower, is constant, namely = 1·16; that is to say, the rate of cooling increases in a geometrical ratio when, for a given excess of temperature of the cooling body, the temperature of an envelope rises in an arithmetical ratio. Hence, if k denotes the rate of cooling corresponding to a given excess of temperature t, when the temperature of the globe is 0°, the rate of cooling corresponding to the same excess of temperature when the temperature of the globe is $\theta°$, will be

$$k \, . \, a^{\theta},$$

where a is the ratio of the rate of cooling when the temperature of the globe is 1° to the rate of cooling when the temperature of the globe is 0°, the excess of temperature being in both cases the same. Making $\theta = 20$, the results contained in the above table give us for $a^{\theta} = a^{20}$ the value 1·16, whence we get $a = \sqrt[20]{1{\cdot}16} = 1{\cdot}0077$. Dulong and Petit found that the dependence of the rate of cooling *in vacuo*, of a heated body, upon its temperature, and its excess of temperature over that of the envelope, might be expressed by the following equation:—

$$\mathrm{A} = \mathrm{M} \, . \, a^{\theta} \, (a^{t} - 1),$$

where A is the rate of cooling, M a constant depending on the mass, extent of surface, and emissive power of the body, and a, θ, and t have the meanings already assigned to them. The numerical value of M in Dulong and Petit's experiments may be deduced from any of the results given in the table: thus, taking $t = 140$ and $\theta = 0$, we have for the rate of cooling $\mathrm{A} = 3{\cdot}88$, and therefore

$$\mathrm{M} = \frac{\mathrm{A}}{a^{\theta}(a^{t} - 1)} = \frac{3{\cdot}88}{1{\cdot}0077^{140} - 1} = 1{\cdot}9829.$$

The values of the constants M and a require to be determined in every case by special experiments; M necessarily varies from one body to another, and it has been proved by De la Provostaye and Desains, that a, or the rate at which the rate of cooling for a constant excess of temperature of 1° increases with rise of temperature, is different for different bodies. If the coefficient a were the same for all bodies, we should have for the rates of cooling of any two bodies under the same circumstances of temperature $\mathrm{A} = \mathrm{M} \, . \, a^{\theta}(a^{t} - 1)$ and $\mathrm{A}^{1} = \mathrm{M}^{1} \, . \, a^{\theta}(a^{t} - 1)$, and therefore

$$\frac{\mathrm{A}}{\mathrm{A}^{1}} = \frac{\mathrm{M}}{\mathrm{M}^{1}} = \text{constant};$$

that is to say, the rates of cooling of the two bodies would be to each other in a constant proportion, so long as they both had the same temperature, and the same excess of temperature over surrounding objects. But the rates of cooling, other things being equal, must depend on the radiating powers of the two bodies, which therefore, under the circumstances above supposed, must be to each other in a constant ratio. To ascertain whether this constant ratio really existed, De la Provostaye and Desains connected a strip of platinum-foil, one face of which was coated with lampblack, and the other with borate of lead, with the terminals of a galvanic battery, so that, by sending through it an electric current of greater or less intensity, its temperature could be raised to any required point, and placed it between two thermo-electric piles, regulating the relative positions so that, when the strip was heated by a moderate current, the effect of its radiation on both piles was exactly the same. On now raising the temperature of the platinum to a higher degree, it was found that this equality of radiation was no longer maintained, the blackened side radiating more heat than the side coated with borate of lead, so that, after the piles had been adjusted to equality of effect with the platinum strip at 100°, they indicated differences in the amount of radiation from its two surfaces in the ratio of 0·75 to 1 when its temperature was 550°. Hence the emissive powers of different substances do not vary according to the same law with variations of temperature, and therefore the quantity denoted above by a is not the same for all bodies.

It was supposed by Newton that the rate of cooling of a given body was directly proportional to the excess of its temperature over that of surrounding objects. It has been already pointed out that Dulong and Petit's experiments prove this not to be the case; nevertheless Newton's law of cooling corresponds very closely with their formula when the value of θ is constant and that of t small, and therefore the factor $a^{t} - 1$, which expresses the effect of the excess of temperature of the cooling body, nearly proportional to t, which denotes that excess. In the cases of most frequent occurrence, in which the law of cooling has to be taken into account,—such, for instance, as the calculation of the corrections to be applied in calorimetrical experiments for differences of temperature between the calorimeter and external objects (see HEAT, iii. 27)—the above conditions are very approximately fulfilled; and hence, in such cases, Newton's law may generally be applied instead of the more accurate, but more complicated, formula of Dulong and Petit.

When a heated body is in contact with air or any other gas, as usually happens in practice, it loses heat not alone by radiation, but also by conduction and communication of heat to the particles of gas. Hence, in such a case, the rate of cooling may be represented by

$$v = A + A_1,$$

where A represents the cooling which is due to radiation, and A_1 the cooling due to conduction, &c. Dulong and Petit found experimentally that the term A_1 may be expressed by the empirical formula

$$A_1 = N \, . \, p^c \, . \, t^{1{\cdot}233},$$

where N is a constant depending on the mass, extent of surface, and nature of the cooling body, and also on the nature of the surrounding gas; p is the pressure of the gas; c is a constant depending on the nature of the gas, being 0·45 for air, 0·38 for hydrogen, and 0·517 for carbonic anhydride; and t is the excess of temperature of the cooling body.

The complete expression for the rate of cooling of any given body whose temperature is $t + \theta$, in a space whose temperature is θ, and in contact with a gas whose pressure is p, is therefore

$$v = M \, . \, a^\theta(a^t - 1) + N \, . \, p^c \, . \, t^{1{\cdot}233}.$$

This equation may be put under a somewhat different form. If we denote the weight of the cooling body by P, its specific heat by C, its superficial area by S, and the quantity of heat given out by a unit of surface in a unit of time by W, we have, for the quantity of heat given out by the whole body in a unit of time,

$$S \, . \, W = P \, . \, C \, . \, v, \text{ and therefore } v = \frac{S \, . \, W}{P \, . \, C}$$

But, since W is made up of two parts, one of which $= w$ is proportional to $a^\theta \, (a^t = 1)$, and the other $= w'$ is proportional to $p^c \, . \, t^{1{\cdot}233}$, we have $\frac{w}{a^\theta(a^t - 1)} = \text{const.} = H$, and $\frac{w'}{p^c \, . \, t^{1{\cdot}233}} = \text{const.} = K$; we may therefore write

$$M = H \, . \, \frac{S}{P \, . \, C} \text{ and } N = K \, . \, \frac{S}{P \, . \, C}$$

and hence

$$v = \frac{S}{P \, . \, C}\left\{H \, a^\theta \, (a^t - 1) + K \, . \, p^c \, t^{1{\cdot}233}\right\},$$

or

$$W = H \, . \, a^\theta(a^t - 1) + K \, . \, p^c \, t^{1{\cdot}233}.$$

In order to apply this formula to special cases, it is necessary to determine, experimentally, the numerical values of the constants H and K. This has been done in the case of several substances by **Hopkins** (Phil. Trans. 1860, p. 379; Proc. Roy. Soc. x. 514), whose principal results are given in the following table, where W expresses, in terms of the quantity of heat required to raise the temperature of 1000 grains of water 1° C., the heat given out by one square-foot of surface in one minute; a, t, θ, and p have the meanings and values already assigned to them, p being measured in metres of mercury:—

Absolute Emissive Powers.

Substances.	Emission per square-foot per minute.
Glass	$W = 9{\cdot}566 \, a^\theta(a^t - 1) + 0{\cdot}03720\left(\frac{p}{0{\cdot}72}\right)^{0{\cdot}45} t^{1{\cdot}233}$
Dry Chalk . . .	$W = 8{\cdot}613 \, a^\theta(a^t - 1) + 0{\cdot}03720\left(\frac{p}{0{\cdot}72}\right)^{0{\cdot}45} t^{1{\cdot}233}$
Dry New Red Sandstone .	$W = 8{\cdot}377 \, a^\theta(a^t - 1) + 0{\cdot}03720\left(\frac{p}{0{\cdot}72}\right)^{0{\cdot}45} t^{1{\cdot}233}$
Sandstone (*building stone*)	$W = 8{\cdot}822 \, a^\theta(a^t - 1) + 0{\cdot}03720\left(\frac{p}{0{\cdot}72}\right)^{0{\cdot}45} t^{1{\cdot}233}$
Polished Limestone .	$W = 9{\cdot}106 \, a^\theta(a^t - 1) + 0{\cdot}03720\left(\frac{p}{0{\cdot}72}\right)^{0{\cdot}45} t^{1{\cdot}233}$
Unpolished Limestone (*same block as the last*)	$W = 12{\cdot}808 \, a^\theta(a^t - 1) + 0{\cdot}03720\left(\frac{p}{0{\cdot}72}\right)^{0{\cdot}45} t^{1{\cdot}233}$

The more recent researches of **De la Provostaye** and **Desains** have served in the main to confirm the accuracy of **Dulong** and **Petit's** formula: but, in order to make it reproduce still more closely the results of observation, they have introduced some modifications; for which we must refer to their original papers. (Ann. Ch. Phys. [3] xvi. 337; xxii. 358.)

Still another circumstance affecting the emissive power of bodies for radiant heat has been pointed out by **Clausius** (Pogg. Ann. cxxi. 43), who arrives by mathematical reasoning at the conclusion that the emissive power of a body depends on the velocity with which rays of heat (or light) are propagated through the surrounding medium, the emissive powers of the same body when immersed in any two media being to each other in the inverse ratio of the squares of the velocities of propagation of radiant heat in those media, or, what comes to the same thing, in the direct ratio of the squares of the indices of refraction of the two media. And by comparing the radiation of heat through hydrogen and through carbonic anhydride, from the blackened surface of a metallic vessel filled with boiling water, v. **Quintus Icilius** (Pogg. Ann. cxxvii. 30), believes that he has obtained an experimental verification of **Clausius's** deduction.

Quality of Emitted Rays.—We have hitherto considered only those circumstances which affect the total intensity of the radiation by heated bodies; but the **quality** of the heat emitted, as well as its quantity, varies with the temperature and nature of the radiating body.

By comparing together the relative penetrating powers of radiant heat from different sources through a great variety of substances, **Melloni** found that, as a general rule, the higher the temperature of the radiating source, the greater was the number of different substances through which a greater or less proportion of the radiated heat was capable of passing. Hence he concluded that the heat radiated by sources of low temperature was more *homogeneous* than the heat radiated by sources of high temperature, the latter containing rays capable of penetrating substances through which none of the rays emitted by sources of low temperature were able to pass. On the theory we have adopted as to the nature of radiant heat, this is equivalent to saying that, among the heat-waves emitted by sources of high temperature, there is a greater variety of wave-lengths than there is among the waves emitted by sources of low temperature. But at the same time that new kinds of rays are successively emitted as the temperature of a radiating body is raised, **Melloni** showed that the rays previously given out by it still continue to be emitted, and with increased intensity. (See *La Thermochrôse*, pp. 311—315.)

By examining, in the manner that has been mentioned, the heat radiated by metals, whether polished, varnished, oxidated, or blackened, as well as by wood, leather, or marble, when each was heated to 160°, **Melloni** was unable to detect any difference of quality (*Op. cit.*, p. 325); but between the heat radiated from a source at 100°, and that radiated from a source at 400°, he found very marked differences. By experimenting in a similar manner, **Knoblauch** could not detect any difference of quality in the heat radiated by such various substances as metals, wood, porcelain, leather, cloth, and cardboard, when heated to temperatures between 30° and 112° (Pogg. Ann. lxx. 352). Moreover, **Draper** (Phil. Mag. [3] xxx. 345) found, by heating very various substances, such as platinum, chalk, marble, fluor-spar, brass, antimony, gas-carbon, and lead, in a gun-barrel, that they all became red-hot, that is to say, they all began to emit red rays, at the same temperature, estimated at 525°; and it has been shown by **Kirchhoff** (Ann. Ch. Phys. [3] lxii. 179), that, on theoretical grounds, such must be the case: that, in fact, *all* bodies whose temperature is gradually raised begin by emitting rays of the same wave-length; at a certain temperature all become red-hot, and at a certain higher temperature, which is the same for all, they begin to emit orange rays, then at a still higher temperature yellow rays, and so on—rays of greater and greater refrangibility making their appearance as the temperature rises. This conclusion is in exact accordance with an experiment long previously made by **Draper** (*loc. cit.*). This consisted in examining, by means of a prism, the rays emitted by a platinum-wire raised to successively higher and higher degrees of incandescence by sending an electric current through it. The first visible rays which the wire emitted were red; then, when the temperature was raised to about 655°, the prismatic appearance of the wire was that of a spectrum extending from the red as far as Fraunhofer's line F in the green (iii. 621); at a temperature estimated as 718°, a narrow strip of blue was visible in addition to the previous colours; at 782° the spectrum reached towards the more refrangible end as far as the line G in the indigo, and at the other end, the portion between the lines B and A which was not visible at first, had made its appearance, thus proving that the emission of rays of greater refrangibility was accompanied by increased intensity of the rays previously emitted. Lastly, at 1165°, the extent of the spectrum was nearly equal to that of daylight.

But although the quality or wave-length of the individual rays which constitute the total radiation from a heated body, depends solely upon the temperature and not upon the nature of the radiating body, the latter circumstance exercises an important influence on the relative intensities of the rays of different wave-length. Comparing radiant heat for a moment to a compound substance, we may say that the radiation from different sources at the same temperature consists of the same component parts, but that these components are not present in all cases in the same relative proportions. Hence when the radiation from different sources at the same temperature is examined as a whole, it sometimes appears to differ not only in intensity, but also in quality: whereas the real difference is in the relative intensity of the rays of particular wave-lengths. It is in this way that we must interpret the observations of De la Provostaye and Desains on the heat radiated from a surface of copper, heated to 173°, one half of which was covered with lampblack, and the other half with cinnabar: observations which proved that the quantity of heat capable of passing through a thin sheet of glass which was radiated by the lampblack, was to the quantity of heat capable of passing through the glass radiated by the cinnabar, as 100 to 67, although the total quantities of heat radiated by the two substances respectively were to each other as 100 to 87. The same remark applies to the experiments of Melloni (*Thermochrôse*, p. 178), Knoblauch (Pogg. Ann. lxxi. 53), and Tyndall (Phil. Mag. [4] xxviii. 527) on the different characters of the heat radiated by certain feebly luminous flames, and by a spiral of platinum-wire made incandescent by the same flames; as well as to Tyndall's experiments (*ibid.* p. 514) on the differences between the radiation from lampblack and platinum at 100°. In certain experiments by Magnus (Pogg. Ann. cxxiv. 476; Phil. Mag. [4] xxx. 81), which appear at first sight to establish a difference of quality, between the heat radiated by polished platinum and by platinum covered with a pulverulent coating of spongy platinum, depending on the nature of the radiating surface, the observed effects were clearly due in reality to difference of temperature, the platinised platinum having a greater emissive power than the bright platinum, and being in consequence more cooled than the latter. Accordingly, the general result of the experiments was that the rays of greatest wave-length (lowest refrangibility) constituted a larger proportion of the total heat radiated by the platinised platinum than of that radiated by the polished metal.

In further illustration of the qualitative differences between the heat radiated by different sources, it may be mentioned that, according to Tyndall's experiments, the proportionate intensity of the rays, whose wave-length is greater than that of red light, to the intensity of the total radiation is as 24 : 25 for the radiation from the brightest part of a flame of coal-gas, as 23 : 24 for the radiation from platinum at a dazzling white heat, and as 9 : 10 for the radiation from the electric light produced by discharging a Grove's battery of 40 cells between carbon points.

In the case of most solid bodies that are sensibly opaque for both light and radiant heat, the emissive power does not exhibit any abrupt variations for rays of different wave-lengths; certain transparent solids, however, have decidedly greater powers of emitting rays of certain determinate wave-lengths, than they have of emitting other rays (*vid. infr.* p. 60). Gases and vapours, on the other hand, generally possess very marked maxima of emissive power corresponding to particular rays: thus, the emissive power of sodium-vapour is incomparably greater for a group of orange-yellow rays, coinciding in refrangibility with Fraunhofer's line D, than for any other visible rays; lithium vapour has a maximum of emissive power for red rays of refrangibility intermediate between Fraunhofer's lines B and C, another, but much smaller maximum for orange rays of somewhat less refrangibility than the line D, and a third, still smaller maximum, for blue rays intermediate in refrangibility, between the lines F and G; potassium-vapour, again, has maxima of emissive power for red rays, equal in refrangibility with the line A, and for violet rays somewhat less refrangible than the line H, while, for nearly all the rays whose refrangibilities are intermediate between those of the lines C and F, it has a low, but almost uniform emissive power (See LIGHT, iii. 622; also SPECTRAL ANALYSIS). About the emissive powers of vapours and gases for rays of lower refrangibility (greater wave-length) than the least refrangible red rays, nothing exact is known; but there is no reason to doubt the essential similarity of their invisible to their visible radiation; and Tyndall has shown that, at temperatures not very greatly exceeding the ordinary temperature of the atmosphere, there are well-marked differences between the emissive powers of different gases and vapours.

Absorption of Radiant Heat.

It has been explained already (p. 43), that when radiant heat arrives at the surface of a material body, part of it is always reflected, either regularly or diffusively; but this reflection is never complete; another portion of the heat penetrates into the substance of the body, and according to the particular properties of the latter, is either wholly or in part transmitted through it, or is wholly or in part annihilated, causing an increase of temperature in the body. It is this extinction of radiant heat in causing rise of temperature in material bodies, that constitutes the phenomenon of absorption. Upon the undulatory theory of radiant heat, we must conceive of it as consisting in the production of vibrations of material particles by the impinging waves of ether. Upon this view, it is obvious that the vibrations excited by radiant heat can never be more rapid than those of the rays themselves, nor, therefore, than those of their source; in other words, a body can never be raised by radiation to a higher temperature than that of the body from which the rays are emitted; and it is likewise obvious that whatever rays a body most plentifully emits, those it will also most plentifully absorb. Both these deductions from theory have received the most complete verification from experiment; in fact the phenomena of absorption have been found to present, even in the minutest particulars, the exact counterpart of those of emission, as upon the undulatory theory they must necessarily do.

The absorptive power of a substance, or its *coefficient of absorption*, is the ratio of the quantity of heat absorbed to the quantity of heat which is incident upon it. Calling the quantity of heat absorbed Q′, and the total quantity of incident heat Q, the coefficient of absorption may be represented by

$$A = \frac{Q'}{Q}$$

If a body absorbed all the heat which fell upon it, its coefficient of absorption would attain a maximum value = 1, but the absorption-coefficient of no known substance quite reaches this maximum, though that of lampblack probably makes a near approach to it.

The experimental measurement of the absorptive powers of different substances is a problem of considerable complexity. The first person to attempt its solution was Sir John Leslie (*Experimental Inquiry into the Nature of Heat*, London, 1804). He coated the bulb of a differential thermometer successively with the different substances to be examined, and observed the temperature which the thermometer attained in each case when it was exposed to the radiation of a source of constant intensity. The results were stated with reference to the absorptive power of lampblack; calling the absorptive power of this substance A_1, and the excess of temperature above the surrounding air attained by the thermometer when its bulb was coated with lampblack t_1, Leslie assumed that the relative absorptive power A of any other substance which caused the thermometer to acquire the excess of temperature t, might be deduced from the equation

$$\frac{A}{A_1} = \frac{t}{t_1}$$

This assumption, however, is not correct. When the thermometer has become stationary at some maximum point of temperature, it is because it is then giving out precisely as much heat as it absorbs. If we denote by Q the constant quantity of heat which falls upon the thermometer, the quantity absorbed in the two cases will be

$$Q \,.\, A \quad \text{and} \quad Q \,.\, A_1\,;$$

and if S is the superficial area of the thermometer-bulb, and E_1 and E the respective emissive powers of lampblack and the substance to be compared with it, we shall have

$$QA = SEt \quad \text{and} \quad QA_1 = SE_1t_1$$

or

$$\frac{A}{A_1} = \frac{E}{E_1} \cdot \frac{t}{t_1}$$

Hence we see that the temperature attained by the thermometer depends on the emissive power as well as on the absorptive power of the substance with which it is coated, and can only be taken as a measure of the former, on the supposition (which we know to be erroneous) that the emissive power of all substances is the same.

A somewhat similar but rather more accurate process was employed by **Melloni**. He coated one side of a thin copper disk, a little larger than the opening of the conical reflector of the thermo-electric pile, with lampblack, and the other side with the substance to be examined, and fixed it close against the open end of the reflector with the blackened side inwards. On now exposing the outer surface of the disk to the radiation from any source its temperature rose, and it consequently itself began to radiate heat from its blackened surface upon the thermo-electric pile: thus causing a deflection of the galvanometer, which, after a certain time, reached a maximum at which it remained constant. Denoting, as before, the quantity of incident heat by Q, the absorptive and emissive powers of the substance by A and E, and the corresponding quantities in the case of lampblack by A_1 and E_1, and further putting S for the area of one side of the disk, we have for the quantity of heat absorbed by the disk QA, and for the quantity of heat emitted by it $SEt + SE_1t$, where t represents the excess of the temperature of the disk above that of surrounding objects. When the temperature of the disk has become stationary, these two quantities of heat are equal, that is

$$Q . A = S(E + E_1) . t;$$

and if both sides of the disk are covered with lampblack, its temperature becomes stationary, when

$$Q . A_1 = 2SE_1 . t_1$$

Hence for the relative absorptive powers, we have

$$\frac{A}{A_1} = \frac{E + E_1}{2E_1} . \frac{t}{t_1}$$

It is evident that the value of the factor $\frac{E + E}{2E_1}$, which appears in this equation, must always lie between the limits ½ and 1, and that it is always more nearly equal to unity than the factor $\frac{E}{E_1}$, which occupies the corresponding place in the equation applicable to Leslie's experiments; in other words, the effects measured by Melloni were more nearly proportional to the absorption-coefficients of the various substances than the effects measured by Leslie. The values of the absorptive powers of various substances, as thus estimated by Melloni, are given in the following table, compared with the absorptive power of lampblack taken as 100:—

Substances.	Sources of Heat.			
	Locatelli's Lamp.	Incandescent Platinum.	Copper at 400°.	Copper at 100°.
Lampblack	100	100	100	100
Indian ink	96	95	87	85
White lead	53	56	89	100
Isinglass	52	54	64	91
Gum-lac	43	47	70	72
Metallic surfaces	14	13·5	13	13

This table shows not only that different substances differ greatly in absorptive power, those substances which have the greatest emissive powers being also the best absorbers, but also that the same substance exerts very different absorbent actions on radiant heat from different sources. And it may be observed that although, for the reasons already stated, the numbers in this table do not represent quite accurately the relative absorptive powers of different substances, they do express accurately the relative absorptive powers of the *same* substance for different kinds of heat. For, if we denote by A and A′ the absorptive powers of the same substance, for the heat from two different sources, and by t and t' the excess of temperature attained by the disk under the radiation from the respective sources, we shall have for the conditions of equilibrium of temperature in the two cases,

$$QA = S(E + E_1) . t \text{ and } QA' = S(E + E_1)t'$$

the difference between t and t' being, under the circumstances of the experiment, so small that we may consider the emissive power of the substance constant, and represent it in each case by E. Hence we get as above:—

$$\frac{A}{A_1} = \frac{E + E_1}{2E_1} . \frac{t}{t_1} \quad \text{and} \quad \frac{A'}{A_1} = \frac{E + E_1}{2E_1} . \frac{t'}{t_1}$$

or,

$$\frac{A}{A'} = \frac{t}{t'}$$

From the foregoing discussion of Leslie's and Melloni's experiments, it will be evident that in order to be able to deduce the absorptive powers of various substances from the elevation of temperature which they undergo under the influence of radiant heat, the conditions of the experiments must be such that the quantity of heat emitted by each substance shall be the same.

These conditions were fulfilled for the first time in the experiments of De la Provostaye and Desains (Ann. Ch. Phys. [3] xxx. 431), the general principle of whose method will be intelligible from the following considerations. If a thermometer, placed inside a closed and exhausted envelope, remains at a constant temperature, it can only be because the quantity of heat which it emits in a given time, is precisely equal to the quantity it absorbs of the heat radiated upon it from the envelope. The quantity of heat emitted in a unit of time is plainly = $v \,.\, P \,.\, c$, if v denotes the rate of cooling of the thermometer under the given conditions of temperature, P its mass, and c its specific heat. Hence, if Q is the quantity of heat radiated by the envelope, and A the coefficient of absorption of the substance,

$$QA = v \,.\, P \,.\, c$$

If now the same thermometer is covered with lampblack, with the absorption-coefficient A_1, the envelope and its temperature remaining unchanged, we have also

$$QA_1 = v_1 \,.\, P \,.\, c$$

and therefore

$$A = A_1 \frac{v}{v_1}:$$

that is to say, the determination of the relative absorbing powers is resolved into a determination of rates of cooling.

In the practical application of these principles, De la Provostaye and Desains employed a very sensitive thermometer with a spherical bulb, which they coated successively with the substances to be examined. The thermometer was fixed in each experiment in exactly the same position in the interior of a metal globe, blackened on the inside, exhausted of air as completely as possible, and kept at a constant temperature by being surrounded with water. In the side of the globe was inserted a convex lens, the focus of which was a little in front of the thermometer-bulb. By means of this lens, the surface of which was so small, compared with the total interior surface of the globe, that it did not make the loss of heat by the thermometer sensibly different from what it would have been if the surface of the globe had been unbroken and of a uniform temperature throughout, the heat of the sun or of a lamp could be concentrated upon the bulb of the thermometer. The temperature of the thermometer then rose, until it became stationary at the point at which the loss of heat by radiation exactly balanced the gain of heat by absorption. The stationary temperature having been found, the rate of cooling corresponding to this temperature was ascertained by separate experiments; and such determinations having been made when the thermometer was coated with several different substances, the coefficients of absorption of these substances could be deduced as above explained. The following table gives the results obtained, compared with the coefficient of absorption of lampblack taken as unity:—

Relative Coefficients of Absorption.

Substance.	Coefficients of Absorption.
Solar heat.	
White lead	0·19
Gold-leaf	0·13
Silver-leaf	0·075
Heat of a "Moderator" lamp.	
Platinum black . . .	1
Cinnabar	0·285
White lead	0·21
Silver, pulverulent . .	0·21
Gold-leaf	0·04

In the case of certain substances, another method is applicable for the determination of their coefficients of absorption, and this method gives absolute values for these coefficients, and not merely comparative values referred to some one substance chosen arbitrarily as a standard. According to what was said above (pp. 43, 44), a quantity of radiant heat Q falling upon a material body is in general broken up into four parts, of which one QA is absorbed, another QT is transmitted, another QR is regularly reflected, while the last QD is diffusively reflected. Hence, we may write

$$Q = Q(A + T + R + D).$$

But, for metallic substances, the power of transmitting radiant heat is imperceptible, and many of them, when thoroughly polished, do not diffuse any sensible quantity of heat. Hence, for perfectly polished metals, T and D in the above equation both become = 0, and, for the coefficient of absorption, we have the expression

$$A = \frac{Q - QR}{Q}.$$

For such substances, therefore, the coefficient of absorption may be found by dividing the difference between the reflected heat and the total incident heat by the incident heat. In this way, De la Provostaye and Desains (*loc. cit.* p. 442) obtained the numbers given in the following table. They remark that they may be considered as applicable to all incidences between 0° and 70°, but that they must be a little in excess of the truth for such metals as cannot be polished sufficiently to completely destroy diffusive reflection:—

Coefficients of Absorption of Polished Metals.

Metal.	Source of Heat.				
	The Sun.	"Moderator" lamp.	Locatelli's lamp.	Flame of alcohol saturated with chloride of sodium.	Copper at 400°.
Steel	0·42	0·34	0·175	0·12	
Speculum metal	0·34	0·30	0·145		
Platinum	0·39	0·30	0·17	0·11	0·105
Zinc	. .	0·32	0·19		
Tin	. .	0·32	0·15		
Brass	. .	0·16	0·07	0·06	0·055
Gold	0·13	. .	0·045	. .	0·045
Plated silver, very bright	0·08	0·035	0·025		

The close agreement between the numbers given in this table and those given in the last for the absorptive powers of gold and silver for solar heat, prove that the numbers of the last table may likewise be taken as very nearly representing the *absolute* coefficients of absorption of the substances included in it, or that the coefficient of absorption of lampblack is very nearly equal to unity, as it is there assumed.

We may mention here an observation of De la Provostaye and Desains which illustrates very strikingly the important influence of the emissive power of a substance as well as of its absorbing power, on the facility with which it is heated by radiant heat. They placed under the receiver of an air-pump a differential thermometer, one of the bulbs of which was covered with gold-leaf, and the other with white lead, a small blackened metallic screen being placed between them in order to intercept their mutual radiation. After the receiver was exhausted, a powerful lamp was placed symmetrically with respect to the two bulbs so as to radiate equally upon each of them, when it was found—notwithstanding the absorptive power of white lead for the heat of the lamp being 0·21 and that of gold-leaf only 0·04—that the gilded bulb was most heated. This, at first sight, paradoxical result is easily understood when it is remembered that, although white lead absorbs five times as much of the heat of the lamp as gold-leaf does, its emissive power for obscure rays is twenty-five times as great as that of gold-leaf.

By comparing the above numbers and those of Melloni (p. 57) with the numbers previously given (p. 48), for the emissive powers of various substances, it will be seen that the best absorbers of heat are also the bodies which radiate most abundantly, while the worst absorbers are also the worst radiaters. And if this comparison is carried further, it is found that the correspondence between the absorptive and emissive powers of bodies is not merely general but exact; that, in fact, any circumstance which modifies the emissive power of a body in any manner whatever, modifies its absorptive power to a precisely similar extent, and in precisely the same way. Thus, taking

Melloni's determinations of the emissive powers of certain substances at 100°, and of the absorptive powers of the same substances for the heat radiated by copper at 100°, we find the following results:—

	Emissive Powers.	Absorptive Powers
Lampblack	100	100
White Lead	100	100
Isinglass	91	91
Indian Ink	85	85
Gum-lac	72	72
Metals	12	13

Again, it has been mentioned (p. 50), that when a heated body is covered with a thin coating of a substance which is more or less transparent for heat, the emissive power increases with the thickness of the superficial film. Precisely similar results have been obtained by Knoblauch in the case of absorption. He covered a metallic plate with layers of varnish, black lac, and white lead of various thicknesses, and found that in each case the absorption increased with the thickness of the layer. In order, however, that this effect may be perceptible, it is necessary that the total thickness should be but small; otherwise the external coating, in consequence of its low conducting power, becomes heated at the surface, and then the increased emission more than counterbalances the better absorption.

The correspondence between emission and absorption naturally extends to visible radiant heat (light), as well as to invisible heat, and in this case many very striking observations in confirmation of it can be made with very simple means. For instance, Balfour Stewart has pointed out (Proc. Roy. Soc. x. 385), that when a black and white china cup is heated in the fire and held in the dark, the parts of the pattern which by daylight are black, in consequence of their absorbing nearly all the visible rays which fall upon them, are more luminous than the parts which by daylight are white, in consequence of diffusively reflecting nearly all the visible rays which they receive. The same observer has also shown that media, which are opaque for certain rays but transparent for others, emit, when heated, rays of the kind for which they are opaque; thus, red glass which absorbs greenish rays, emits greenish rays when heated and viewed in the dark; while green glass, which absorbs red rays, emits red rays. The emission and absorption of rays of the same wave-length is still more strikingly exhibited by gaseous bodies. It has been already stated (p. 55), that these substances usually emit rays of certain definite degrees of refrangibility, or length of wave, with much greater intensity than other rays, and it has been proved by Kirchhoff that the rays which a gas or vapour most readily absorbs are precisely those which it most freely emits (see LIGHT, iii. 622). The identity in the absorbing and emitting properties of the same body has been found to hold good even in respect to the state of polarisation of the rays absorbed or emitted. Thus at ordinary temperatures a plate of tourmaline, cut with faces parallel to the principal axis of the crystal, transmits, with little diminution of intensity, rays polarised in a plane perpendicular to the axis, but absorbs almost completely rays which are polarised in a plane parallel to the axis (iii. 655); and Kirchhoff (Ann. Ch. Phys. [3] lxii. 186) has found, not only that this difference of action on differently polarised rays is retained, though in a less degree, at temperatures at which tourmaline itself becomes luminous, but that the light which the crystal then emits is polarised in the same manner as the light which it absorbs. The same fact was independently observed, at about the same time by Stewart (Proc. Roy. Soc. x. 503), who also showed that the absorption and radiation of heated tourmaline are equal in degree as well as in kind.

Among the non-luminous rays, differences of refrangibility are not recognisable by any character so distinctly marked as the various colours which reveal such differences in the case of the visible rays; hence, at temperatures below that at which they become luminous, it is less easy to demonstrate that the rays which particular substances give out are identical in quality with those which they absorb. Nevertheless the following observations seem to prove conclusively that such is the case. Colourless rock-salt, which is perfectly transparent for visible rays, is likewise so transparent for the invisible rays emitted by a surface of lampblack at 100°, that a plate of rock-salt 0·77 inch thick allows 75 per cent. of them to pass, whereas the same plate allows only 30 per cent. to pass of the heat radiated by rock-salt at 100°. Similarly, a thin plate of crown-glass allows only half as much heat from heated crown-glass to pass as from heated lampblack. (B. Stewart. *Op. cit.* p. 387.)

It has also been shown by Tyndall (Phil. Mag. [4] xxviii. 518) that aqueous vapour is specially opaque for the heat of a hydrogen flame, wherein the principal radiater is no doubt aqueous vapour; that carbonic anhydride is especially opaque for the heat of a carbonic oxide flame; and sulphurous anhydride for the heat radiated by the flame of sulphide of carbon.

From the foregoing facts, we may conclude that the difference between the two processes of emission and absorption of radiant heat, is a difference of the kind which would be represented in mathematics by a difference of sign. The mechanism of the two processes, if we may use the expression, appears to be absolutely identical, but in the one case it operates in the opposite sense to what it does in the other.

The equality of emission and absorption may be deduced from the fact that a body which is in equilibrium with surrounding objects undergoes no change of temperature when the condition of its surface is changed. A thermometer, for instance, is not affected by wrapping its bulb in muslin; and since in this case its emissive power is greatly increased, its temperature can be maintained unaltered by the same quantity of heat falling upon it from without, only if its power of absorbing this heat is increased in exactly the same proportion.

Transmission of Radiant Heat.

In previous parts of this article, we have already had occasion several times to speak of the differences exhibited by various bodies in respect of their power of transmitting radiant heat, and of the differences shown by the same body in its power of transmitting heat from various sources. Before proceeding to a somewhat more detailed consideration of the phenomena of transmission, it will be convenient to explain certain terms that are often employed in the description of them. These terms were introduced by Melloni to facilitate the conception and expression of the fact, first clearly established by his own researches, that the relations of the invisible rays of heat to material bodies, are essentially identical with those of light. Bodies which, like atmospheric air, rock-salt, glass, &c.—afford a more or less free passage to rays of heat, are called by Melloni diathermic; while those which like the metals, entirely obstruct the passage of radiant heat, are called adiathermic; the corresponding properties, which we have hitherto in this article spoken of as *transparence* and *opacity* for radiant heat, being called diathermacy and adiathermacy, sometimes also diathermaneity and adiathermaneity. The property of *selective transmission* which most diathermic bodies possess, that is the property of transmitting rays of certain wave-lengths, and not transmitting other rays, is called thermochrose (from θερμὸν and χρῶσις), and bodies which possess this property are termed thermochroic, and those which do not possess it athermochroic. The terms thermochrose and thermochroic are, however, also used in reference to sources of heat in whose radiation rays of certain wave-lengths predominate, and to the heat itself which such sources give out, as well as to adiathermic bodies which exhibit a power of selective absorption or reflection: just as, in the case of light, the words *colour*, *coloured*, &c., are used equally in speaking for instance, of the flame of alcohol charged with chloride of sodium, of the light which such a flame gives out, of a piece of yellow glass, or of a piece of gold, and the same word, *yellow*, is used to describe the light itself, the flame which emits it, the glass which transmits it, and the metal which reflects it.

By maintaining a constant source of heat at a constant distance from the thermo-electric pile, and interposing between them various substances in succession, Melloni was able to determine, on the one hand, the influence of the transmitting substance on the quantity of heat transmitted; and by placing different sources of heat at such distances from the thermo-electric pile that each caused the same deflection of the galvanometer, and interposing the same substance on the path of the rays from each source, he was able, on the other hand, to measure the influence of the source of heat on its transmission. The following tables contain the results of a large number of experiments of this kind.

The four sources of heat employed in the experiments, the results of which are given in the first table, were—1st, an oil-lamp (Locatelli's), with a solid square wick and without chimney; 2nd, a spiral of platinum-wire heated to incandescence in the flame of a spirit-lamp; 3rd, a plate of copper covered with lampblack, and heated to about 400° by the flame of a spirit-lamp applied to the back of it; 4th, a cubical copper vessel coated with lampblack, and filled with water at 100°. The next table gives in like manner the intensity of the heat of an Argand oil-lamp, provided with a glass chimney, after passing through a thickness of 9·21 millimetres of certain liquids, enclosed between plates of glass, the intensity of the incident heat being taken as 100:—

Transmission of Radiant Heat by Solids.

Substances. (Reduced to a common thickness of 2·6 millimetres.)	Percentage of Heat transmitted—from			
	Locatelli's lamp.	Incandescent platinum.	Copper at 400°.	Copper at 100°.
Rock-salt (limpid)	92·3	92·3	92·3	92·3
Sulphur (Sicilian, yellow)	74	77	60	54
Fluor-spar (limpid)	72	69	42	33
Rock-salt (translucent)	65	65	65	65
Beryl (greenish-yellow)	54	23	13	0
Fluor-spar (greenish)	46	38	24	20
Iceland spar (limpid)	39	28	6	0
" " (limpid)	38	28	5	0
Glass (limpid)	39	24	6	0
" (limpid)	38	26	5	0
Rock-crystal (limpid)	38	28	6	3
" " (smoky)	37	28	6	3
Potassic bichromate (orange)	34	28	15	0
Topaz (limpid)	33	24	4	0
Carbonate of lead (limpid)	32	23	4	0
Sulphate of barium (translucent)	24	18	3	0
Felspar (adularia; translucent)	23	19	6	0
Amethyst (violet)	21	9	2	0
Artificial amber (yellow)	21	5	0	0
Beryl (aquamarine; bluish-green)	19	13	2	0
Agate (yellow, translucent)	19	12	2	0
Sodic borate (translucent)	18	18	8	0
Tourmaline (dark-green)	18	16	3	0
Gum (common; yellowish)	18	3	0	0
Heavy spar (veined, translucent)	17	11	3	0
Selenite (limpid)	14	5	0	0
Citric acid (limpid)	11	2	0	0
Ammonic carbonate (translucent streaked)	12	3	0	0
Potassio-sodic tartrate (limpid)	11	3	0	0
Amber (natural; yellow)	11	5	0	0
Alum (limpid)	9	2	0	0
Glue (yellowish-brown)	9	2	0	0
Sugarcandy (limpid)	8	1	0	0
Fluor spar (dark green, veined)	8	6	4	3
Melted sugar (barley-sugar? yellowish)	7	1	0	0
Ice (limpid)	6	0·5	0	0

Transmission of Radiant Heat by Liquids.

Name of Liquid. (Thickness of stratum = 9·21 millimetres.)	Percentage of Heat transmitted from Argand lamp with glass chimney.
Bisulphide of carbon (colourless)	63
Bichloride of sulphur (dark garnet-red)	63
Phosphorous chloride (colourless)	62
Chloroform (colourless)	37
Nut-oil (yellow)	31
Oil of turpentine (colourless)	31
Oil of rosemary (colourless)	30
Colza-oil (yellow)	30
Olive-oil (greenish-yellow)	30
Rock-oil (brownish-yellow)	28
Balsam of copaiba (yellowish-brown)	26
Oil of lavender (colourless)	26
Poppy-oil (yellowish-white)	26

Transmission of Radiant Heat by Liquids (continued).

Name of Liquid. (Thickness of stratum = 9·21 millimetres.)	Percentage of Heat transmitted from Argand lamp with glass chimney.
Rectified naphtha (colourless)	26
Ether (pure; colourless)	21
Sulphuric acid (pure; colourless)	17
Nordhausen sulphuric acid (brown)	17
Solution of ammonia (colourless)	15
Concentrated nitric acid (colourless)	15
Absolute alcohol (colourless)	15
Hydrate of potassium (colourless)	13
Rectified acetic acid (colourless)	12
Pyroligneous acid (brown)	12
Solution of sugar (concentrated, colourless)	12
Solution of rock-salt (colourless)	12
Solution of alum (colourless)	12
White of egg (yellowish-white)	11
Distilled water	11

The following short table gives the quantities of heat transmitted through a layer of water 50 millimetres in thickness, contained between highly polished plates of glass, according to the experiments of De la Provostaye and Desains (Ann. Ch. Phys. [3] xxx. 286). These results illustrate very well the influence which the source of heat exerts upon the relative proportion in which it is able to pass through the same medium. The numbers of this table represent the intensity of the heat transmitted from each source, the intensity of the incident heat being in each case taken as = 100:—

Transmission of Radiant Heat through Water

Source of Heat.	Percentage transmitted.
The Sun. Solar rays which had already passed through 52 centimetres of water	92
The Sun. Total Solar radiation	58
Argand lamp. Rays which had already passed through a lens and 10 centimetres of water	51
Electric light (carbon points)	23 to 24
Lime made incandescent in the flame of ether fed with oxygen	20
The Sun. Invisible rays from a part of the spectrum as far beyond the red as the distance between red and the limits of the green and blue	14
Locatelli or Argand lamp with chimney	10
Flame of alcohol saturated with chloride of sodium	2 to 3
The Sun. Invisible rays still less refrangible than the above	0·

After the explanations that have been already given, the results recorded in the above tables do not call for much further discussion. We must, however, direct attention to the remarkable properties of rock-salt in relation to radiant heat. It will be seen that, according to Melloni's experiments, a plate of clear colourless rock-salt transmits the same proportion (92·3 per cent.) of the heat which falls upon it, from whatever source. Hence Melloni concluded that rock-salt exerts no absorbing power whatever on heat-rays of any kind, or that it is in fact perfectly diathermic and athermochroic. The 7·7 per cent. by which the intensity of the incident rays is diminished by passing through a plate of rock-salt, Melloni attributed to the effect of reflection at the surfaces of entrance and exit, not to absorption within the substance of the plate; for if this loss were due in whole or in part to absorption, its amount could hardly have been the same for heat from sources so greatly differing in temperature. This conclusion is supported by the further observation of Melloni, that the quantity of heat transmitted by perfectly clear and transparent rock-salt is independent of its thickness, being always 92·3 per cent. of the heat incident upon it; whereas if two plates of rock-salt are used instead of one, in which case the number of reflecting surfaces is doubled, the percentage of heat transmitted is reduced to $\frac{92{\cdot}3}{100} \times \frac{92{\cdot}3}{100} =$ 85·2. According, however, to the more recent experiments of De la Provostaye and Desains (Compt. rend. xxxvi. 84, 1073), as well as of Tyndall (Phil. Mag. [4] xxviii. 532), rock-salt does exert a slight but perceptible absorbent action upon rays from sources of low temperature, and an experiment of **Stewart's** has been already mentioned (p. 60) which shows it to be opaque to a great extent for rays emitted by rock-salt.

In the case of all other substances except rock-salt, the thickness of the transmitting stratum, as well as the nature of the source of heat, has a great influence on the amount of heat transmitted. The effect of variations of thickness was made by **Melloni** the subject of an extended experimental investigation, but, before giving the numerical results arrived at by him, it will be well to explain the theoretical investigation of the same subject by **Biot** (*Mém. de l'Académ. des Sciences*, xiv. 466.—**Daguin's** *Traité élémentaire de Physique*, ii. 62). Suppose a pencil of rays of sensibly the same wave-length to fall perpendicularly upon a plate of some diathermic substance and let the intensity of the pencil be represented by I, the reflecting power of the surface of the plate by r, and the thickness of the plate by e. Then a pencil of the intensity Ir will be reflected at the first surface, and the intensity of the pencil which enters the plate will be $I(1 - r)$. Of this, a certain proportion will undergo absorption while traversing the plate, the amount of absorption being some function $f(e)$ of the thickness, which has to be determined. The quantity of heat which arrives at the second surface will therefore be $I(1 - r)f(e)$. Here a second reflection will take place, whereby a fraction r' of this heat will be kept back, and the quantity which issues from the plate will consequently be

$$I(1 - r)(1 - r')f(e).$$

If a second plate of the same substance, having the thickness e', be placed in the path of the pencil emergent from the first plate, the intensity of the heat which issues from the second plate will be found, by reasoning similar to the above, to be

$$i = I(1 - r)^2(1 - r')^2 f(e) f(e').$$

Now let the same original pencil pass through a single plate, still of the same substance, but of the thickness $e + e'$; the intensity of the emergent pencil will be found as above, to be

$$i' = I(1 - r)(1 - r')f(e + e').$$

But it is found by experiment that $i = i'(1 - r)(1 - r')$, that is to say, that the loss by absorption is the same for the same thickness of substance, whether this is disposed in two plates or united into one, the factor $(1 - r)(1 - r')$ representing the additional loss by reflection in the former case. Hence we have

$$f(e + e') = f(e) \cdot f(e'),$$

which can only hold good if $f(e) = a^e$, where a is a constant dependent on the nature of the substance and on that of the incident rays, so that $f(e) \cdot f(e') = a^e \cdot a^{e'} = a^e + a^{e'}$. Consequently, the expression for the quantity of heat which passes through a plate of the thickness e is

$$I(1 - r)(1 - r')a^e,$$

which shows that *the intensity of the transmitted heat varies according to a geometrical progression when the thickness of the plate increases in an arithmetical progression.* The ratio, a, of the former progression, which depends as we have said on the nature of the plate and of the incident heat, is called the *coefficient of transmission* of the substance of which the plate is made, for the particular kind of heat in question; it represents the quantity of heat transmitted through a thickness of 1 millimetre.

It follows also from the above considerations, that the quantities of heat absorbed by successive layers of equal thickness of the same substance likewise form a diminishing geometrical progression; for, calling the intensity of the heat which penetrates the first surface of the substance I', we get, for the quantities transmitted and absorbed by successive layers of the same thickness, the following expressions:—

	Transmitted.	Absorbed.
By the *first* layer . . .	$I'a$	$I' - I'a = I'(1 - a)$
By the *second* layer . .	$I'a^2$	$I'a - I'a^2 = I'a \cdot (1 - a)$
By the *third* layer . . .	$I'a^3$	$I'a^2 - I'a^3 = I'a^2 \cdot (1 - a)$
⋮	⋮	⋮
By the n^{th} layer . . .	$I'a^n$	$I'a^{n-1} - I'a^n = I'a^{n-1} \cdot (1 - a)$

If the incident pencil consists of rays of various wave-lengths, having the respective intensities $I, I_1, I_2, \ldots$ and if the coefficients of transmission of the diathermic plate for these various rays are respectively $a, a_1, a_2, \ldots$ the intensity of the pencil on emerging from a plate of the thickness e will be the sum of the intensities of the rays of each several wave-length, and will therefore be represented by—

$$(1 - r)(1 - r')(Ia^e + I_1 a^{1e}, + I_2 a_2^e + \ldots).$$

Hence it is evident that the composition or *thermochrose* of the emergent pencil will not be the same as that of the incident pencil except when the coefficients a, a_1, a_2, &c. are all equal. We shall see immediately that each of these deductions from theory is fully confirmed by experiment.

The results of **Melloni's** experiments on the transmission of heat through layers of varying thickness are collected in the following table:—

Transmission of Radiant Heat through layers of various Thicknesses.

Thickness in millimetres.	*Glass* from St. Gobin.			Limpid *Rock-crystal*			Smoky *Rock-crystal.*			*Colza Oil.*		Distilled *Water.*	
	Locatelli's lamp.	Incandescent platinum.	Copper at 400°.	Locatelli's lamp.	Incandescent platinum.	Copper at 400°.	Locatelli's lamp.	Incandescent platinum	Copper at 400°.	Locatelli's lamp.	Incandescent platinum.	Locatelli's lamp.	Incandescent platinum.
0·5	77·5	62·1	14·4	78·6	69·5	14·8	81·7	70·0	15·4	64·0	32·0	25·1	8·7
1·0	73·3	51·5	9·9	76·8	65·1	11·3	78·6	65·0	12·3	48·3	22·8	19·3	5·7
1·5	70·4	46·1	6·7	74·8	62·5	9·7	. .	. .	. .	41·0	18·7	16·0	4·2
2·0	68·2	42·8	5·0	73·3	60·6	8·7	75·1	60·3	9·1	36·1	16·3	13·9	3·2
2·5	66·6	. .	. .	72·5	. .	. .	. .	. .	. .	32·7			
3·0	65·3	38·3	2·9	71·8	57·6	7·3	73·1	57·4	7·8	30·6	13·6	11·4	2·0
4	63·4	35·8	2·0	70·8	55·3	6·6	71·4	54·8	7·0	27·8	12·6	10·0	1·5
5	62·0	34·0	1·5	70·2	53·3	6·0	. .	. .	. .	25·7	10·8	9·1	1·1
6	60·9	32·3	1·4	69·8	51·4	5·3	. .	. .	. .	23·9	9·8	8·6	1·0
7	60·0	30·9	1·2	69·5	49·8	5·0	. .	. .	. .	22·6	8·9	8·2	0·8
8	59·2	29·7	1·1	69·3	48·4	4·6	. .	. .	. .	21·8	8·1	8·0	0·6
9	. .	. .	. .	. .	. .	. .	. .	. .	. .	21·2	7·5	7·8	0·5
10	. .	. .	. .	. .	. .	. .	. .	. .	. .	21·0	7·1	7·7	0·4
11	. .	. .	. .	. .	. .	. .	. .	. .	. .	20·9	6·7	7·7	0·3
50	. .	. .	. .	. .	. .	. .	. .	. .	. .	12·5	2·1	2·4	0·0
86	. .	. .	. .	. .	. .	. .	59·0	35·0	0·7				
100	. .	. .	. .	. .	. .	. .	. .	. .	. .	8·1	1·2	1·3	0·0
150	. .	. .	. .	. .	. .	. .	. .	. .	. .	6·1	. .	0·7	0·0
200	. .	. .	. .	. .	. .	. .	. .	. .	. .	5·3			

By subtracting the quantity of heat transmitted by a layer of n millimetres in thickness from that transmitted by a layer of $n - 1$ millimetres, we obtain the quantity of heat *absorbed* by the n^{th} stratum of 1 millimetre thick. Thus, for instance, for the absorption of the heat of a Locatelli's lamp by successive strata of water, 1 millimetre in thickness, we obtain the following results:—

Number of each stratum . .	1	2	3	4	5	6	7	8
Quantity of heat absorbed . .	80·7	5·4	2·5	1·4	0·9	0·5	0·4	0·2

Here the diminution of absorption in successive strata of the same thickness is very apparent, but the ratio of the absorption of a given stratum to the absorption of the previous one is by no means constant, as, according to the foregoing discussion, must be the case for homogeneous heat. The reason of this is, that the heat employed in the experiments was far from homogeneous, but consisted in part of visible and in part of invisible rays, and each of these portions contained rays differing greatly from one another in wave-length. Consequently, the coefficient of transmission of water for visible rays being nearly equal to unity, but very much less for invisible rays, the different component parts of the heat underwent unequal absorption, and hence the quality of the heat which arrived at each stratum was different from that of the heat which arrived at the preceding and the succeeding strata. When, however, homogeneous heat is used, the absorption in successive equal strata of the same material takes place according to a regularly decreasing geometrical series. This is clearly shown in the following experiments by **Masson** and **Jamin** (**Wüllner's** *Lehrbuch der Experimentalphysik* ii. 336). The constituent rays of a beam of solar heat were separated from each other by means of a rock-salt prism, and a portion of the yellow rays of the spectrum so produced was allowed to fall upon one, two, or three pieces of the same yellow glass of equal thickness, and the intensity of the emergent rays was measured in each case. Representing the thickness of each piece of glass by e, and its coefficient of transmission for the rays in question by a, we find the following values:—

For the heat transmitted by 1 piece of yellow glass $= A_1 = I\,(1 - r)\,(1 - r')\,a^e$,

For the heat transmitted by 2 pieces of yellow glass $= A_2 = I\,(1 - r)^2\,(1 - r')^2\,a^{2e}$,

For the heat transmitted by 3 pieces of yellow glass $= A_3 = I\,(1 - r)^3\,(1 - r')^3\,a^{3e}$.

The same beam of yellow rays was next allowed to fall upon one, two, or three thicknesses of clear colourless glass, whose coefficient of transmission was nearly equal to unity, and the intensity of the heat transmitted in each case was determined. Calling these quantities of heat respectively B_1, B_2, and B_3, we have—

$$B_1 = I(1-r)\ (1-r');\ B_2 = I(1-r)^2(1-r')^2, \text{and } B_3 = I(1-r)^3(1-r')^3;$$

$$\text{and consequently } \frac{A_1}{B_1} = a^e;\ \frac{A_2}{B_2} = a^{2e};\ \text{and} \frac{A_3}{B_3} = a^{3e}.$$

The coefficients of transmission for one, two, and three thicknesses of yellow glass were thus found, independently of the effects of reflection at the surfaces. The square-root of the second and the cube-root of the third ought obviously to be equal to the first, if the calculation was made with perfect strictness, and the following numerical results show that such was nearly the case:—

Number of Plates of Glass.	Heat transmitted.	a^e.
1	$a^e = 0{\cdot}497$	0·497
2	$a^{2e} = 0{\cdot}2097$	0·458
3	$a^{3e} = 0{\cdot}094$	0·455

The gradual decrease in the value of a^e is to be attributed to the coefficient of transmission for colourless glass having been taken as exactly equal to unity, whereas in reality it is only nearly so.

The following table, taken from Melloni (*Thermochrôse*, p. 227), illustrates on the other hand, the change of quality which a pencil of non-homogeneous radiant heat undergoes on passing through diathermic substances. The numbers in the table represent the intensities of the transmitted pencils compared to that of the incident pencil taken as 100. The original source of heat was a Locatelli's lamp, and the thickness of the plates, except where otherwise stated, was 2·6 millimetres:—

Transmission of Radiant Heat through Two Media.

Substances interposed.	Direct radiation.	Percentage transmitted of the heat of a Locatelli's lamp after passing through a plate of				
		Rock-salt.	Alum.	Potassic bichromate.	Gypsum.	Opaque black glass (1·85 mm. thick).
Rock-salt . . .	92·3	92·3	92·3	92·3	92·3	92·3
Fluor-spar . . .	78	78	90	88	91	91
Beryl	54	53	80	66	91	57
Iceland spar . .	39	40	91	56	89	55
Glass (0·5 mm. thick) .	54	54	90	68	85	80
Glass (8 mm. thick) .	34	33	90	47	82	45
Rock-crystal . .	38	39	91	52	85	54
Potassic bichromate .	34	33	57	71	53	24
Sulphate of barium .	24	25	36	25	47	57
White agate . .	23	23	70	30	78	17
Felspar (adularia) .	23	22	23	43	58	23
Yellow amber . .	21	20	65	20	61	8
Opaque black glass (1·8 mm. thick) .	16	16	0	14	18	52
Opaque black mica (0·9 mm. thick) .	20	20	0	16	12	43
Yellow agate . .	19	19	57	24	64	14
Aquamarina . .	19	18	60	26	57	21
Borax . . .	18	18	23	23	33	24
Green tourmaline .	18	17	1	14	10	30
Common gum . .	18	18	61	12	52	4
Gypsum . . .	14	14	59	22	54	15
Gypsum (12 mm. thick)	10	10	56	17	45	0·5
Carbonate of ammonium . . .	12	12	44	11	34	5
Citric acid . . .	11	10	88	16	52	2
Potassio-sodic tartrate	11	11	85	15	60	1
Alum . . .	9	9	90	15	47	0

It will be observed that, of the five substances through which the heat of the lamp was caused to pass in these experiments, rock-salt is the only one which did not materially alter its properties; all the other substances having strongly marked thermochroic characters, or transmitting rays of different wave-lengths with very unequal facility (as may be seen from the table on page 62), emit heat of decidedly different composition from that which falls upon them. Two of these substances indeed, alum and black glass, are to a great extent of opposite thermochroic properties: of the heat emergent from the plate of alum, 90 per cent. was able to pass through a second plate of the same material, but none of it was able to pass through a plate of black glass; while of the heat emergent from the latter body, 52 per cent. was transmitted by a second plate of the same kind, but none at all was transmitted by a plate of alum. Alum, although almost perfectly transparent for visible rays, is in very moderate thicknesses completely opaque for the invisible heat-rays; hence, as shown by the table on page 62, it completely intercepts the heat radiated by sources at temperatures below visible redness. In this property alum closely resembles ice, and it probably owes it in great measure to the large proportion of solidified water (of crystallisation) which it contains. Black glass, on the other hand, is very opaque for visible rays, and relatively transparent for invisible rays. Hence, to some extent, it filters off the visible rays, and allows heat richer in rays of great wave-length to pass. This effect, however, is produced much more completely by blackened rock-salt, or better still, as Tyndall has shown (Phil. Mag. [4] xxviii. 333), by a solution of iodine in bisulphide of carbon. Such a solution, though perfectly opaque for luminous rays, does not absorb any appreciable quantity of the rays of greater wave-length. Hence, by placing a cell filled with this liquid on the path of a beam of rays from a powerful electric lamp, Tyndall has succeeded in cutting off completely the luminous rays, and obtaining a beam of invisible heat-rays of very much greater intensity than has ever been obtained in any other way.

By comparing the absorbing and transmitting powers of various substances in the liquid and vaporous states, Tyndall has arrived at the important conclusion that the numbers by which these properties are measured are to each other in the same relative proportion in the case of vapours, as in the case of the liquids from which those vapours are formed (Phil. Mag. [4] xxviii. 451). The following tables contain some of the results on which this conclusion is founded; the numbers express the percentage of the incident heat *absorbed*, the source of heat being a platinum wire heated by an electric current:—

Absorption of Radiant Heat by Liquids.

Liquid.	Thickness of liquid in parts of an inch.				
	0·02	0·04	0·07		0·27
Sulphide of carbon .	5·5	8·4	12·5	15·2	17·3
Chloroform . .	16·6	25·0	35·0	40·0	44·8
Methylic iodide .	36·1	46·5	53·2	65·2	68·6
Ethylic iodide . .	38·2	50·7	59·0	69·0	71·5
Benzene . . .	43·4	55·7	62·5	71·5	73·6
Amylene . . .	58·3	65·2	73·6	77·7	82·3
Ether . . .	63·3	73·5	76·1	78·6	85·2
Ethylic acetate .	. .	74·0	78·0	82·0	86·1
Ethylic formate .	65·2	76·3	79·0	84·0	87·0
Alcohol . . .	67·3	78·6	83·6	85·3	89·1
Water . . .	80·7	86·1	88·8	91·8	91·0

Absorption of Radiant Heat by Vapours.

Name of Vapour.	Platinum spiral.			
	Barely visible.	Brightly red-hot.	White hot.	Near fusion.
Sulphide of carbon . . .	6·5	4·7	2·9	2·5
Chloroform	9·1	6·3	5·6	3·9
Methylic iodide	12·5	9·6	7·8	
Ethylic iodide	21·0	17·7	12·8	
Benzene	26·3	20·6	16·5	
Amylene	35·8	27·5	22·7	
Ether	43·4	31·4	25·9	23·7
Ethylic formate	45·2	3 ·9	25·1	21·3
Ethylic acetate	49·6	34·6	27·2	

That the quality of the absorption of the same substance may remain constant, notwithstanding great changes of physical condition, is proved by the observation of Bunsen (Ann. Ch. Pharm. cxxxi. 255), that phosphate of didymium in a state of igneous fusion shows the same absorption-band in the yellow as that which characterises didymium-salts in aqueous solution. (See ii. 322.)

From the great absorbing power of water, as shown in the first of the above tables, and from the general correspondence which is apparent between the absorbing powers of liquids and their vapours, it appears probable that aqueous vapour would have a relatively high absorbing power. This view is taken by Tyndall, and is supported by the results of a great number and great variety of apparently conclusive experiments, from which he infers that, "weight for weight, aqueous vapour transcends all others in absorptive power." It is, however, proper to add that Magnus, who has also devoted a great deal of attention to the same point, differs widely from Tyndall in his estimate of the absorptive power of aqueous vapour, regarding it as very much lower; and so long as the source of the divergence in the results of these two experimenters remains unexplained, the question between them cannot be considered as decided.

The transmission of radiant heat through permanent gases has also been investigated by Tyndall, who has found that these substances differ very greatly in their power of absorbing heat from sources of low temperature. The following table gives the relative absorbing powers found by him for a column 32 inches long of several gases, under a pressure of 760 millimetres, for the heat radiated from a plate of copper heated by a Bunsen's gas-lamp:—

Name of gas.	Absorption. (That of air = 1)	Name of gas.	Absorption. (That of air = 1)
Air	1	Carbonic anhydride	90
Oxygen	1	Nitrous oxide	355
Nitrogen	1	Marsh-gas	403
Hydrogen	1	Sulphurous anhydride	710
Chlorine	39	Ethylene	970
Hydrochloric acid	62	Ammonia	1195

When the same gases are compared in shorter columns, or under lower pressures, the difference in their relative absorbing powers becomes even more strikingly evident.

There is one other circumstance, besides the nature of the medium and the wave-length of the rays, which affects the transmission of radiant heat. This is the *amplitude* of the vibrations, or the intensity of individual rays. It has been already stated (p. 54) that, as the temperature of a radiating body is raised, it gives out rays of smaller and smaller wave-length, but that the amplitude of the more slowly vibrating rays, which it gave out at first, is increased at the same time. This is very distinctly proved by some experiments of Tyndall (Phil. Mag. [4] xxviii. 334), from which it appears that the intensity of the invisible radiation (capable of passing through an opaque solution of iodine in bisulphide of carbon) of a spiral of platinum-wire may be increased four-hundredfold by raising the temperature of the wire from a dark heat to a dazzling white heat. Hence the non-luminous rays of luminous sources are not, in all respects, equivalent to the rays of the same wave-length from non-luminous sources; and Tyndall accordingly found that 20 per cent. of the non-luminous rays of the electric lamp passed through a layer of concentrated solution of alum more than an inch thick, although alum and its solution, even in much thinner layers, are quite opaque for the same rays emitted from sources of lower temperature.

The *temperature* of the medium has not been clearly proved to exert any influence on the transmission of radiant heat. According to Wilhelmy (Ann. Ch. Phys. [3] xlvii. 206), glass transmits the rays of an Argand lamp more abundantly when hot than when cold; but De la Provostaye and Desains failed to detect any difference in the transmission of rock-salt or glass at ordinary temperatures, or at 150°. (Daguin, *Traité de Physique*, ii. 52.)

CONDUCTION.

If one part of a material body is at a higher temperature than the rest, the high temperature of this part can be maintained, and the temperature of other parts can be prevented from rising, only by the action of external causes. If the body is left to itself, it will sooner or later acquire a uniform temperature throughout, the hot part losing heat and the colder parts gaining heat. This tendency towards equalisation of temperature throughout any continuous portion of matter, manifests itself in the phenomena of conduction of heat, the property of bodies which is known as their con-

conducting power or **conductivity** being the rapidity with which this equalisation is effected under certain specified conditions. The different degrees of this property in different bodies, as exhibited by the various lengths of time during which equal differences of temperature can be maintained between equally distant parts, are so striking and familiar that there is no need to draw attention to the mere fact of their existence.

The laws of the conduction of heat have been investigated in relation to the two cases of conduction through a plate or wall with parallel surfaces, and of practically unlimited area, and of conduction in a prismatic or cylindrical bar. For these two cases the connection of conducting power with the distribution of temperatures has been investigated mathematically, especially by **Fourier** (*Théorie analytique de la Chaleur*, Paris, 1822) and **Poisson** (*Théorie mathématique de la Chaleur*, Paris, 1835), but we cannot attempt to do more here than to give the principal results that have been arrived at experimentally.

The **coefficient of conductivity** of a substance is defined as *the quantity of heat which passes in a unit of time through a plate of that substance of unit thickness and unit area, whose surfaces are maintained at constant temperatures differing from one another by one degree.* This coefficient has been measured experimentally by three processes, which differ from each other in principle as well as in the manner in which they have been carried out. The most direct process is that adopted by **Peclet** (Ann. Ch. Phys. [3] ii. 107), which consisted in measuring the time required for a given quantity of heat to pass through plates of different materials of definite thickness, the two surfaces being maintained at known constant temperatures. The last condition was attained by keeping the two sides of the plate bathed with water, which, however, it was found needful to agitate very briskly, in order to make sure that the film of water in actual contact with the plate was of the same temperature as the remainder. When the water at one side of the plate was at 25° C., and that at the other side at the temperature of the air, the times required for the same elevation of temperature to be produced in the water at the cooler side, with plates of lead of 20 mm. and 15 mm. thickness, were 500 and 380 seconds respectively, or very nearly proportional to the thicknesses of the plates (20 : 15 = 500 : 375). From experiments of this kind, **Peclet** calculated the number 3·84 for the coefficient of conductivity of lead, expressing thereby the number of kilogramme-water-degrees of heat which pass through a plate of lead 1 millimetre thick, and 1 square-metre in superficial area, in 1 second, when a constant difference of temperature of 1° C. is maintained between the two surfaces. For scientific purposes, it is commonly more convenient to express conducting powers in gramme-water-degrees, *per* second, *per* centimetre of thickness, *per* square-centimetre of surface; the numerical value of coefficients expressed upon the scale is, however, the same as when they are referred to **Peclet's** unit.

By a method essentially similar in principle, but different in the manner of its execution, **Lucien De la Rive** (Ann. Ch. Phys. [4] i. 504) has found for the conducting power of glass the number 0·13, and by a comparative method he ascertained the conducting power of ice to be 1·75 times that of glass: hence, in the same units, the coefficient of conductivity of ice is expressed by the number 0·23.

Calvert and **Johnson** (Phil. Trans. 1858; Proc. Roy. Soc. ix. 169) have also made experiments in order to determine in a similar manner the conductivities of several metals and alloys; but their method was not such as to make their numerical results of great value.

When once the coefficient of conductivity of a substance is known, the quantity of heat Q, which passes through a layer of the substance of the thickness e and area s, in the time T, when its two surfaces are kept at the constant temperatures t° and t'° supposing that these temperatures have been maintained unaltered long enough for the body to have arrived at a stationary condition of temperature throughout its whole thickness, and that none of the heat which enters the first surface escapes elsewhere than at the opposite surface, may be expressed by the following formula:—

$$Q = ks \,.\, \frac{t - t'}{e} \,.\, T, \ldots (1)$$

where k stands for the coefficient in question. Calling $\frac{Q}{T}$, or the quantity of heat which passes in a unit of time, the *strength of the thermal current* = S, and $\frac{e}{ks}$ the *thermal resistance* of the substance, the above formula may be written $S = \frac{t - t'}{R}$, in which form it is seen to be exactly analogous to **Ohm's** formula for the strength of [illegible] the difference of temperature [illegible] being the condition [illegible] and [illegible] comparable with the electromotive [illegible]

The [illegible] within a body can remain constant only when [illegible] as it receives; [illegible] following stratum, [illegible] quantity of heat passing [illegible] in a given time must be the same [illegible] temperature [illegible] strata [illegible] the same amount. Hence in such a case as we have supposed [illegible] successive strata of the substance from [illegible] surface [illegible] that of [illegible] surface [illegible] and [illegible] distance from the latter surface of any given stratum the temperature of this stratum will be expressed by [illegible]

[illegible]

[illegible] stratum of particles is not [illegible] and distribution of [illegible] instance when [illegible] any given stratum of particles [illegible] and so its own [illegible] heat to the next stratum, [illegible] heat as fast [illegible] the more [illegible] and [illegible] has been reached, the [illegible] of the heat which [illegible] successive [illegible] and increases [illegible] the farther [illegible] analogous to the [illegible] successive parts [illegible]

[illegible] a quantity [illegible] conducting power [illegible]

[illegible] and suppose the [illegible] And [illegible] the quantity of heat which [illegible] where the temperature [illegible] the surface remains constant we have [illegible] within equal to the amount imparted [illegible] defines k when k is known.

The remaining methods by which the [illegible] conductivity has been measured may be [illegible] distribution of temperature in [illegible]. This [illegible] be a function of the coefficient [illegible] other things equal, it must necessarily be [illegible] in a bad one, and less uniform in a [illegible] conductivity is high, than in one for which the coefficient [illegible]

mode of experiment depending [illegible] maintaining a temperature at one end [illegible] examined, [illegible] the temperature of the bar at various points [illegible] after the high temperature of the heated end has been kept up long enough for the temperature at every other point to have become invariable. Experiments of this kind were made by **Rumford**, who placed one end of an iron bar in boiling water and surrounded the other with ice; and observed its temperature at three points, equidistant from each other, and from the two ends, by means of three delicate thermometers inserted in holes bored in the side of the bar, and filled up with mercury to render the indication of the temperature more exact. More extensive determinations were made in the same way by **Biot** and afterwards by **Despretz** (Ann. Ch. Phys. [2] xix. 97; xxxvi. 422) and **Gouillaud** (*ibid.* [3] xlviii. 47). From these experiments it results that the temperatures of successive strata of a uniform bar heated at one end *decrease in geometrical progression when the distances from the source increase in arithmetical progression.* From the ratios of the progression for various substances, the ratios of their coefficients of internal conductivity could be calculated, when the coefficients of external conductivity were made the same for all, by giving to each substance the same condition of surface, and making the external medium also the same. But when bars of considerable section are used, the interior of each cross-section must necessarily be at a sensibly higher temperature than the sides, and the holes bored for the insertion of the thermometers must also have affected the results. Hence **Langberg** (Pogg. Ann. lxvi. 1; Ann. Ch. Pharm. lvi. 189) experimented upon various metals in the form of wire, determining their temperatures at different points by means of a small thermo-electric pile applied in contact with them. This method of experimenting was afterwards improved by **Wiedemann** and **Franz** (Pogg. Ann. lxxxix. 497), who made by it the most extensive and, there is little doubt, the most accurate series of observations on the relative conducting powers of various metals that have yet been published. The following table contains the relative conducting powers of the metals examined by them, compared with that of silver taken arbitrarily as 100, and also the absolute conducting powers of the same metals, calculated from their relative numbers by means of **Peclet's** determination of the absolute conductivity of lead (p. 69):—

Conductivity of Metals.

Name of Metal.	Coefficient of Conductivity.		Name of Metal.	Coefficient of Conductivity.	
	Relative.	Absolute.		Relative.	Absolute.
Silver . . .	100	45·2	Iron . . .	11·9	5·38
Copper . . .	73·6	33·4	Lead . . .	8·4	3·84
Gold . . .	53·2	24·0	Platinum . .	8·5	3·79
Brass . . .	23·1	10·4	German silver .	6·3	2·85
Zinc . . .	19·0	8·6	Rose's fusible metal	2·8	1·26
Tin . . .	14·5	6·55	Bismuth . .	1·8	0·81

The relative conducting powers of various rocks have been determined by **Hopkins** (Proc. Roy. Soc. viii. 535). His method of experimenting consisted in placing a cylindrical block of the substance to be examined, with its base just in contact with the surface of mercury contained in a shallow pan, and heated to a constant known temperature, and observing, when the distribution of heat within the block had become stationary, the excess of temperature above the surrounding air attained by a shallow stratum of mercury covering the upper face of the block—precautions being of course taken to prevent loss of heat through the sides of the block, and any disturbing effect of radiation from the heating apparatus. The observed excesses of temperature evidently depended directly upon the internal conductivities of the substances examined, and (inversely) upon the external conductivity of mercury. It has been shown (p. 70) that when the temperature of the surface of a body, whose temperature increases inwards, remains constant, the relation expressed by the following equation holds between its coefficients of internal conductivity k, and external conductivity h:—

$$\frac{k}{h} = \frac{t' - \theta}{t - t'}e.$$

In **Hopkins'** experiments, the external conductivity of mercury ($= c$) took the place of h in the above formula in the case of every substance; k, however, varied from one substance to another. Hence, by putting into the formula the observed values of t, t', θ, and e, the value of $\frac{k}{c}$ could be ascertained. The following are some of the results obtained for substances in the state of dry powder:—

Chalk	0·056
Clay	·07
Sand	·15
Sand and clay	·11

These values are proportional to the absolute internal conducting powers of the several substances, but in order to deduce these conducting powers from them, they require to be multiplied by the unknown absolute value of c, the external conducting power of mercury.

The observation of the distribution of temperature in a mass whose temperature is changing has been employed by Forbes (Trans. Roy. Soc. Edinb. xvi. 206), Ångström (Pogg. Ann. cxiv. 513; Ann. Ch. Phys. [3] lxvii. 379), and Neumann (Ann. Ch. Phys. [3] lxvi. 183) for the determination of coefficients of conductivity. Forbes' investigation related to the rate of penetration downwards into the earth of the solar heat received by the surface. The general effect of the seasons is that the temperature of the surface of the ground oscillates (in Britain) between a maximum which occurs in July or August, and a minimum occurring in January or February. If now the earth's crust were a perfect conductor of heat, the yearly maximum and yearly minimum of temperature would occur at any point below the surface, at the same epochs as they do at the surface itself, and the yearly range of temperature would be as great below the surface as above it. But the earth's crust opposing in reality a very considerable resistance to the propagation of heat, the maxima and minima occur later below the surface (for instance, at a depth of 25·6 feet in the porphyritic trap of the Calton Hill, Edinburgh, the annual maximum occurs in December or January, and the minimum in June or July), and the difference between them, or the yearly range of temperature, is less than it is at the surface. Thus the oscillation of temperature which occurs at the surface suffers a *retardation of phase* and a *diminution of amplitude* as it advances inwards. From these two effects, as revealed by the observation of thermometers sunk to various depths, Forbes was able to deduce the absolute coefficients of conductivity of the strata in which the thermometers were buried.

A method precisely the same in principle has since been employed by Ångström for the determination of the conductivities of certain metals. Square bars of the metals to be examined were alternately heated and cooled at one place, and after a considerable number of such alternations the distribution of temperature was observed by means of thermometers inserted into the bars at intervals of 50 millimetres from each other.

Neumann's method depended on observations of the course of cooling in bars which had been heated at one end until their temperature became stationary throughout, or in cubes or spheres of five or six inches diameter which had been previously heated to a uniform temperature.

The following table gives some of the results obtained by Ångström and by Neumann, reduced to the gramme-water-second-centimetre unit:—

Coefficients of Conductivity.

Substance.	Ångström.	Neumann.
Copper	91·03	110·75
Zinc	. .	30·70
Brass	. .	30·19
Iron	16·30	16·37
German-silver	. .	10·94

The numbers in the following table give the values referred to the same unit, of the ratio $\frac{k}{cD}$ according to Neumann's experiments, k being the coefficient of internal conductivity, c the specific heat, and D the density of the several substances:—

Substances.	$\frac{k}{cD}$
Coal	0·116
Melted sulphur	·143
Ice	1·144
Snow	·367
Frozen earth	·916
Sandstone	1·357

Neumann finds that the conductivity of the same substance varies very sensibly with the temperature.

It will be observed that while the ratios of the conductivities of the metals found by Neumann agree on the whole with the relative conductivities determined by Wiedemann and Franz, they considerably exceed the absolute conducting powers calculated from these by means of Peclet's coefficient for lead. On the other hand, the absolute coefficients obtained by Neumann and Angström for iron are nearly identical, and this value might therefore perhaps be most safely taken in order to convert Wiedemann and Franz's relative numbers into absolute coefficients.

In substances whose elasticity or structure is different in different directions, the rate at which heat is propagated depends upon the direction. Thus in crystals not belonging to the regular or cubical system (CRYSTALLOGRAPHY, ii. 121), Sénarmont has shown that the conducting power in the direction of the principal axis is generally either a maximum or a minimum. If a source of heat be imagined at the centre of such a crystal, the heat would be conducted outwards with different velocities in different directions, and consequently the points which at any moment possessed a common temperature, would be situated on the surface of an ellipsoïd; and Sénarmont found that the axes of the *isothermal ellipsoïds* of crystals coincide with their optic axes. He also found that mechanical strains or pressures are capable of modifying the conducting power of bodies for heat in the directions in which they are applied.

Wood presents somewhat similar phenomena. It was observed by De la Rive and De Candolle that the conducting power of wood is always greater along than across the fibre. These observations were extended by Knoblauch, who showed that, as a rule, the difference of conducting power is least in the hardest and greatest in the softest kinds of wood. Thus in boxwood the ratio of the axes of the isothermal ellipsoïd is 1·25 : 1, in walnut it is 1·45 : 1, in apricot-tree 1·6 : 1, and in soft woods (such as poplar, lime, birch, pine), it is 1·8 : 1. Tyndall has carried the same investigation still further: he finds that at all points not situate in the centre of the tree, wood possesses three unequal axes of calorific conduction, which are at right-angles to each other. The first and principal axis is parallel to the fibre of the wood; the second and intermediate axis is perpendicular to the fibre and to the ligneous layers; while the third and least axis is perpendicular to the fibre, and parallel to the layers.

When two different metals are in contact, the rate of propagation of heat is different on the two sides of the surface of separation, and therefore if heat is flowing across this surface the law of the variation of temperature is different at the two sides of it; but Wiedemann has shown that, when the contact is perfect, there is no finite difference between the temperatures of the surfaces of the two metals which touch each other.

Conduction of Heat by Liquids.—In consequence of the diminution of density which takes place almost universally in liquids when they are heated, an increase of temperature is rapidly communicated by convection to the whole of a quantity of liquid, when heat is applied to it from below. Hence it was formerly supposed that liquids possessed a high degree of conductivity for heat. Rumford however showed, near the beginning of this century, that when heat is imparted to a liquid from above, so that the expansion of the heated portions cannot cause them to rise and so produce a circulation of the liquid, the communication of heat from one part of a liquid to another takes place with extreme slowness, so much so indeed that he concluded that liquids are entirely without any real conducting power for heat. Later observers nevertheless, and especially Despretz, have proved that liquids do conduct heat in the same way as solid bodies, but for the most part very much more slowly. Despretz, in fact, found that when a constant source of heat acts for a long time upon the upper part of a column of water, the heat gradually penetrates downwards; and that when the distribution of temperature in the column has become stationary, the excess of temperature above that of the surrounding air decreases according to a geometrical progression, when examined at points whose depths below the surface increase in arithmetical progression. Hence it follows that the law of conduction in water is the same as the law of conduction in metals, and by comparing Despretz's results for water with those he obtained for copper, it appears that the conductivity of water is to that of copper as 9 to 1000.

Conduction of Heat by Gases.—The distribution of heat in gases certainly takes place chiefly by convection, as it does in liquids, but several observers have concluded that they do nevertheless possess a feeble power of conduction. The most direct experiments on this subject are due to Magnus (Pogg. Ann. cxii. 497); according to them it appears that hydrogen, if not other gases, has a certain degree of conductivity. This conclusion accords with the results of a mathematical investigation of the propagation of heat in gases by Clausius (Phil. Mag. [4] xxiii. 532), who finds that the conducting power of the lighter gases must exceed that of the heavier gases. As a provisional estimate, he gives for the conducting power of air about $\frac{1}{1400}$ of that of lead as determined by Peclet, and for the conducting power of hydrogen about four times that of air. G. C. F.

RADICLES, or **RADICALS.** The notion of compound radicles, as it is at present received in chemical science, has been explained already in previous articles (CLASSIFICATION, i. 1014—1017; EQUIVALENTS, ii. 495; FORMULÆ, RATIONAL, ii. 700); all that is necessary here is therefore to indicate briefly the origin of the idea, and the principal modifications which it has undergone.

The word "radical" is of constant occurrence in the writings of Lavoisier. For him and for his school, chemistry consisted mainly in the investigation of oxygen and its combinations. Compound bodies were divided into the two fundamental classes of acids, which were supposed to owe their essential properties to their containing a large proportion of oxygen, and salifiable bases, which were regarded either as simple bodies or as containing a small proportion of oxygen. In all cases the presence or absence of oxygen, or the proportion of it which a compound body contained, was considered the most important point in its chemical history, and as chiefly determining its properties. In the case of the acids especially, the oxygen, which all were supposed to contain, was looked upon as the sole cause of their characteristic properties; whether the oxygen was combined with sulphur, with phosphorus, or with nitrogen, was regarded as a matter of far less importance. Hence arose the necessity for adopting some common designation for the various substances which were capable of serving as foundations or nuclei upon which oxygen could attach itself, and thus give rise to acids; it was in this sense that the word *radical* was first employed in chemistry. "Il faut donc," said Lavoisier, "distinguer dans tout acide la base acidifiable à laquelle M. de Morveau a donné le nom de radical, et le principe acidifiant, c'est-à-dire, l'oxigène." (*Traité élémentaire de Chimie*, édit. 1789, vol. i. p. 69.) The passage here referred to appears to be in Section ii. "*Des bases acidifiables ou principes radicaux des acides*" of de Morveau's "Mémoire sur le Développement des Principes de la Nomenclature méthodique" (1787). The definition of a radical which is here given is interesting, not only in connection with our present subject, but for the light it throws on the views then entertained with respect to the constitution of acids. After speaking of the acids of nitrogen, carbon, sulphur, and phosphorus, de Morveau goes on to discuss the nomenclature of acids of unknown composition, such as muriatic acid, boracic acid, the acid of vinegar, &c., with regard to which he says: "Nous nous sommes contentés de désigner l'être simple qui y modifie l'oxigène par l'expression de *base acidifiable*, ou, pour abréger, de *radical* de tel acide; afin de garder la même analogie, et de pouvoir considérer à leur tour chacun de ces êtres d'une manière abstraite."

The signification of the word *radical* was soon somewhat extended by Lavoisier. Two years after the publication of de Morveau's memoir, he says: "J'ai déjà fait observer que dans le règne minéral, presque tous les radicaux oxidables et acidifiables étoient simples; que dans le règne végétal au contraire, et surtout dans le règne animal, il n'en existoit presque pas qui ne fussent composés du moins de deux substances, d'hydrogène et de carbone; que souvent l'azote et le phosphore s'y réunissoient, et qu'il en résultoit des radicaux à quatre bases." (*Traité élémentaire*, vol. i. p. 209.) The idea of compound radicles, which we meet with in this passage, occurs very frequently in other parts of the same work, and it is of importance to observe that it is applied to explain the constitution of neutral bodies as well as of acids. This is still more distinctly seen in other passages; thus, of sugar, gum, and starch, it is said (*Op. cit.* pp. 125, 126): "Ces trois substances ont pour radical l'hydrogène et le carbone combinés ensemble, de manière à ne former qu'une seule base, et portés à l'état d'oxide par une portion d'oxygène; ils ne diffèrent que par la proportion des principes qui composent la base." Elsewhere it is suggested that the *oils* may actually constitute compound organic radicles in the free state, thus (pp. 198, 199): "On aperçoit aisément que les huiles étant composées d'hydrogène et de carbone, elles sont de véritables radicaux carbone-hydreux ou hydro-carboneux, et en effet il suffit d'oxygéner les huiles pour les convertir d'abord en oxides, et ensuite en acides végétaux, suivant le degré d'oxygénation. On ne peut pas cependant assurer d'une manière positive que les huiles entrent toutes entières dans la composition des oxides et des acides végétaux; il est possible qu'elles perdent auparavant une portion de leur hydrogène ou de leur carbone, et que ce qui reste de l'une et de l'autre de ces substances ne soit plus dans la proportion nécessaire pour constituer des huiles." Again (pp. 210, 211): "Doit-on conclure de ces réflexions, que les huiles soient la base, qu'elles soient le radical des acides végétaux et animaux? J'ai déjà exposé mes doutes à cet égard. Premièrement, quoique les huiles paroissent n'être uniquement composées que d'hydrogène et de carbone, nous ne savons pas si la proportion qu'elles en contiennent est précisément celle nécessaire pour constituer les radicaux des acides. Secondement, puisque les acides végétaux et animaux ne sont pas seulement composés d'hydrogène et de carbone, mais que l'oxygène entre également dans leur combinaison, il n'y a pas de raison de conclure qu'elles contiennent plutôt de l'huile que de l'acide carbonique et de l'eau. Ils contiennent bien, il est vrai, les matériaux propres à chacune de ces combinaisons ; mais ces combinaisons ne sont point réalisées à la température habituelle dont nous jouissons, et les trois principes sont dans un état d'équilibre, qu'un degré de chaleur, un peu supérieur à celui de l'eau bouillante, suffit pour troubler." This last passage is especially worthy of notice, as showing that Lavoisier distinctly apprehended that the question of what radicle a given complex body contained, involved not only a knowledge of its composition, but also of its constitution, or of the way in which its constituent elements were combined.

The further development of the notion of compound radicles was a consequence of the advance of organic chemistry. Consequently, with the exception of Gay-Lussac's discovery of cyanogen in 1815, we hear little more of either the word or the idea until about the year 1832. It is true that in 1817 Berzelius repeated Lavoisier's statement that all inorganic oxides have simple radicles, and all organic oxides compound radicles; but this remained a general doctrine without precise special application, until, in 1832, Liebig and Wöhler showed that, by regarding oil of bitter-almonds and its derivatives as compounds of a radicle containing C^7H^5O, they became exactly comparable with the compounds of potassium or other metals. This view of the constitution of the benzoyl-compounds was at first eargerly adopted by Berzelius (Ann. Pharm. iii. 282), but was afterwards modified by him on the ground that it was inconsistent with the electro-chemical theory to suppose that oxygen could be a constituent of a radicle. He consequently represented these compounds as containing the radicle $C^{14}H^5$; for instance, benzoic acid, $C^{14}H^5.O^3 + HO$, chloride of benzoyl, $2(C^{14}H^5.O^3) + C^{14}H^5.Cl^3$. The formulæ thus obtained were strictly comparable with those adopted by Berzelius for corresponding inorganic compounds: *e.g.* chromic acid, $CrO^3 + HO$, oxichloride of chromium, $2CrO^3 + CrCl^3$. (See *Berzelius' Jahresbericht*, xiii. 203 [1833]; xviii. 358 [1838]; xix. 345 [1839]).

The next class of bodies to which formulæ were given, founded on the idea of their containing compound radicles, exactly similar to elements in their mode of combination, were the derivatives of alcohol. Alcohol itself was represented by Berzelius (*Jahresbericht*, xiii. 195) as the oxide of the radicle CH^3, and ether as containing the radicle C^2H^5: thus, alcohol $2(CH^3)O$, ether $2(C^2H^5)O$, chloride of ethyl $C^2H^5.Cl$, &c. Liebig soon afterwards (1834) gave the name *ethyl* to the radicle C^2H^5, and represented alcohol as its hydrated oxide (Ann. Pharm. ix. 1; Pogg. Ann. xxxi. 335; Berzel. Jahresber. xv. 343). In 1835, Regnault represented aldehyde, acetic acid, Dutch-liquid, and several of its derivatives as compounds of the radicle C^2H^3, to which he gave the name *aldehydene* (Ann. Ch. Phys. [2] lviii. 301, and lix. 358; also Ann. Pharm. xiv. 22, and xv. 60), and which was afterwards (Jahresber. xvii. 232 [1837]) called *acetyl* by Berzelius; and in the few following years, similar views were applied by Berzelius and the chemists of his school to nearly all known organic compounds. In all cases the leading idea was that which was thus expressed by Dumas in 1837 (Compt. rend. v. 300; Journ. pr. Chem. xiv. 298; Berzel. Jahresber. xviii. 243): "In mineral chemistry the radicles are simple; in organic chemistry they are compound: herein is the only difference between them; the laws of combination and of transformation are the same in both. Even if the radicles of inorganic chemistry, such as sulphur, the metals, and oxygen, are really compound, we cannot look forward to their decomposition; for if this decomposition is possible, it requires forces which we are not acquainted with. In organic chemistry the case is the reverse, and the difficulty is less. Here the radicles are compound, and our whole art consists in treating them so that they are not broken up into their elementary constituents. This decomposition, however, we can foresee and prevent, for it takes place according to easily apprehended laws; so that it is by no means difficult to recognise an organic radicle, and to transfer it undecomposed from one compound to another."

These views were not, however, the only ones that were applied to organic compounds. Mitscherlich, for instance, regarded a certain number of organic bodies as constituted quite differently from any known inorganic compounds (see FORMULÆ, ii. 701, 702); and Laurent, in 1836, proposed a general theory of the constitution of organic compounds, which was entirely inconsistent with the radicle theory as above described (see NUCLEUS THEORY, iv. 143). But the chief opposition to the radicle theory arose,—(1), from the difficulty of reconciling with it, as it was held by Berzelius, its chief supporter, the constitution of substances, such as chloracetic acid, formed by the action of chlorine and its analogues on organic bodies; (2) from the fact that of the very numerous radicles whose existence the theory assumed, scarcely two or three were known in the separate state; and (3) in consequence of Gerhardt and Laurent's discovery that the number of atoms of hydrogen, chlorine, nitrogen, and their analogues, taken together, which was contained in a molecule of any well-investigated compound, was always an *even* number, whereas all the supposed compound radicles contained an *odd* number of such atoms.

We have not space to trace the long and bitter controversies which arose upon each of these points: an excellent account of them will be found in **Kekulé's** *Lehrbuch der organischen Chemie* (vol. i. pp. 59–94, 1859). It must suffice to say here that the objections to the "radicle" theory, referred to under the first of the above heads, arose from its identification with the electro-chemical theory, and therefore lost their force when this theory was abandoned, and it was consequently admitted that radicles playing the part of electro-positive metals might contain not only oxygen, but chlorine, bromine, or in fact any other element. The discovery of cacodyl by **Bunsen** in 1842, of methyl, ethyl, and butyl by **Frankland** and **Kolbe** in 1849, and subsequently of several other of the so-called alcohol-radicles, which at first sight seemed to afford a conclusive answer to all *à priori* objections against the possible existence of radicles in the free state, resulted in its being proved that the molecules of the isolated radicles consisted of two atoms, and thus the "law of even numbers" received a confirmation instead of the expected refutation. (See Alcohol-radicles, i. 96.)

The idea of compound radicles, as it is now entertained, is quite independent of the question whether they can be actually prepared in the separate state or not. A radicle, in modern chemical language, is simply a group of elements which is common to a more or less numerous series of allied compounds, and remains unaffected by the processes whereby these compounds are transformed one into another. It is essentially correlative with the idea of molecular types; and, as pointed out in the places referred to at the beginning of this article (especially ii. 700), the radicle which any complex compound is regarded as containing, must depend upon the type to which the compound is referred, while, conversely, the type is equally dependent on the radicle.

G. C. F.

RADIOLITE. Natrolite, from Brevig in Norway (iv. 29): see also an analysis by **Michaelson**. (Jahresb. 1863, p. 819.)

RADISH. *Raphanus sativus.* Radish-roots contain, according to **T. J. Herapath** (Chem. Gaz. 1847, p. 279), in 1000 pts.:—

Water	959·74	Red colouring-matter	1·77
Woody fibre	17·02	Fat oil	0·40
Nitrogenous substance with a little starch	2·04	Sinapine?	0·04
Albumin	0·91	Alkaline and earthy phosphates, with a little gypsum	0·74
Extractive matter	2·26	Acetates of potassium and sodium	0·22
Gum	4·30	Nitrates of potassium and sodium	5·17
Sugar	1·14	Chlorides of potassium and sodium	4·16

The ash of the root and herb of the radish has also been analysed by **T. Richardson** (Jahresb. 1847–48, Table C to page 1074), with the following results:—

	K^2O.	Na^2O.	CaO.	MgO.	SO^3.	SiO^2.	P^2O^5.	$Fe'''PO^4$	KCl.	$NaCl$.	
Root	21·16	. .	8·78	3·53	7·71	8·17	40·09	2·19	1·29	7·07	= 99·99
Herb	5·05	11·09	27·90	7·08	9·64	8·22	6·07	16·45	. .	8·50	= 100·00

The dried root yielded 6·43 per cent., and the dried herb 2·76 per cent. ash.

RADISH, OIL OF. The roots and seeds of the radish yield, by distillation with water, a milky liquid, from which an essential oil may be obtained by rectification. This oil is colourless, heavier than water, contains sulphur, forms a white precipitate with mercuric chloride, yellow with platinic chloride. It is moderately soluble in water.

The same oil is obtained by distilling, with water, the seeds of *Brassica Napus*, *Cochlearia Draba*, and *Cheiranthus annuus*.

RAMALINA CALICARIS. A lichen which yields alpha-usnic acid. (See Usnic Acid.)

RAMMELSBERGITE. Trimetric arsenide of nickel, $NiAs^2$ (iv. 36).

RANDANITE. An earthy hydrate of silica, occurring near Pont Gibaud in France. (See Opal, iv. 304.)

RANGOON TAR. See Naphtha (iv. 3).

RANUNCULUS. The root of *Ranunculus Ficaria*, gathered in Tuscany in April and May, was found by **Toscani** (Cimento, v. 453) to contain 0·5 to 1·0 per cent. crystallisable sugar, 0·4 to 0·6 dextrin, 28 starch, and an acrid deleterious substance.

The acrid juice of *Ranunculus sceleratus* yields by distillation a clear, sharp-tasting, fetid liquid, which when kept for some time, even in closed vessels, deposits a white amorphous precipitate of anemonin (i. 290). Ether extracts from this distillate a neutral, acrid, golden-yellow, non-sulphuretted oil, heavier than water, which attacks the eyes strongly, and raises blisters on the skin. When kept under water, or in contact with chloride of calcium, it concretes to a white solid mass, which quickly changes into anemonin and anemonic acid. It is to this transformation of the acrid principle of the ranunculus, and not to its volatility, that the loss of acridity of the plant by drying is due. (Erdmann, J. pr. Chem. lxxv. 209.)

RAPAKIVI. A variety of granite containing 60·46 per cent. orthoclase, 31·83 quartz, and 6·71 mica, occurring at Pyterlaks and other localities in Finland. (Jahresb. 1862, p. 784.)

RAPE. See BRASSICA (i. 654).—Rape-seed oil, *Huile de navette*, is a fat oil obtained by pressure from the seeds of winter-rape (*Brassica Napus*), which yield about 33 per cent of it. This oil is yellow, has a peculiar odour, a density of 0·9128 at 15°, and solidifies at a few degrees below 0°. By dry distillation, it yields a mixture of volatile fatty acids, acrolein, and oily hydrocarbons of very variable boiling point. These hydrocarbons are strongly attacked by nitric acid, yielding caprylic, œnanthylic, caproic, valerianic, butyric, propionic, and acetic acids. With chromic acid the same hydrocarbons yield only acetic and propionic acid. (Schneider, Ann. Ch. Pharm. lxx. 107.)

Rape-seed oil is used for illumination, for the manufacture of soft soaps, for oiling woollen stuffs, in the preparation of leather, and for lubricating machinery.

The seeds of summer-rape, *Brassica præcox*, yield a yellow viscid oil of specific gravity 0·9139, which deposits tallow at −8°, and solidifies to a yellowish-white butter at −10°. (Schübler.)

The seeds of the turnip, *Brassica Napus*, yield a smaller quantity of a similar oil, of specific gravity 0·9167.

Colza oil, used chiefly for illumination, is obtained to the amount of about 33 per cent. from the seeds of colza or wild navew, (*Brassica campestris*, var. *oleifera*). It is yellow, of specific gravity 0·9136 at 15°, and solidifies at −6°. It is chiefly a mixture of two glycerides, which yield, by saponification, two peculiar fatty acids. (See BRASSIC ACID, i. 655.)

RAPHANOSMITE. Kobell's name for native selenide of lead and copper from Tilkerode (iii. 557.)

RAPHANUS. (See RADISH, p. 76.)

RAPHILITE. Asbestiform tremolite from Lanark, in Canada. (See HORNBLENDE, iii. 169.)

RASTOLYTE. A reddish-grey micaceous mineral occurring in monoclinic forms at Monroe, Orange County, New York, analysed by Shepard (Sill. Am. J. [2] xxiv. 128), and by Pisani (Compt. rend. liv. 606; Jahresb. 1862, p. 749), whose results differ widely from one another:—

SiO^2.	Al^2O^3.	FeO.	CaO.	MgO.	Alkali and loss.	H^2O.		
42·3	6·5	38·25	2·0	1·0	6·15	3·8*	= 100	(Shepard).
34·98	21·88	28·44	. .	6·24	. .	9·22	= 100·76	(Pisani).

From the physical characters of the mineral, Pisani regards it as allied to ripidolite.

RATANHIA. In the bark of ratanhia or rhatany-root, *Krameria triandra*, Wittstein (Jahresb. 1854, p. 656) found a peculiar iron-greening tannin, a body analogous to cinchona-red, or rather to quinova-red, resulting from the decomposition of the tannin; also gummy and extractive matters, wax, sugar, starch, and oxalate of calcium. In the American extract of ratanhia, Wittstein found a nitrogenous body, which he regarded as tyrosine. (See the next Article.)

RATANHINE. $C^{10}H^{13}NO^3$. (E. Ruge, Viertelj. d. naturforsch. Gesellsch. in Zürich, vi. Heft 3; Jahresb. 1862, p. 493.)—A compound homologous with tyrosine ($C^9H^{11}NO^3$), occurring to the amount of 1·26 per cent. in the extract of rhatany-root. It was first observed by Wittstein, who regarded it as tyrosine. To prepare it, the solution of rhatany extract is precipitated with basic acetate of lead; the filtrate, freed from lead by sulphydric acid, is evaporated to a small bulk; the crystals, which separate after 12 hours, are pressed, washed, and dissolved in ammonia; the solution is left to evaporate; and the crystals which then separate are further purified by precipitating their solution with basic acetate of lead, and treating the filtrate with sulphydric acid at the boiling heat.

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* With fluorine.

Ratanhine, thus purified, crystallises in large spherical aggregates of delicate white needles, drying up to an interlaced mass. It dissolves in 125 pts. of boiling water, and, like tyrosine, has a great tendency to form supersaturated solutions. It is slightly soluble in boiling spirit of ordinary strength, quite insoluble in absolute alcohol and in ether. It is not precipitated by neutral or basic acetate of lead, or by mercuric acetate. A solution of ratanhine saturated at 15°, assumes a rose-red colour when heated with a few drops of *mercuric nitrate*, and on further addition of the latter, deposits brown-red flocks. When ratanhine triturated with a small quantity of water is mixed by drops with dilute *nitric acid*, and heated to the boiling-point, the liquid becomes rose-red, then ruby-red, then gives off gas and assumes a deep indigo-blue colour, due to the formation of resinous bodies. This coloration is perceptible even to the 50,000th degree of dilution. With a larger quantity of nitric acid, more complete decomposition takes place. Ratanhine moistened with water is coloured rose-red to violet-red by *nitrous acid*, and with a larger quantity of water, a blue or green solution is ultimately formed.

Ratanhine, like tyrosine, unites both with mineral acids and with alkalis: it decomposes the carbonates of the alkaline earths. A solution of ratanhine in baryta-water deposits part of the ratanhine unaltered, while the compound $C^{10}H^{11}Ba''NO^3$ remains dissolved.

Hydrochlorate of ratanhine, $C^{10}H^{13}NO^3.HCl$, crystallises by spontaneous evaporation in colourless acid prisms or laminæ, which are decomposed by water or alcohol, with separation of ratanhine.

Ratanhine-sulphuric or *Sulpho-ratanhic acid*.—The dark-red solution of ratanhine in 5 pts. of warm concentrated sulphuric acid becomes colourless on dilution, and if then neutralised with carbonate of barium, deposits slender silky needles of the salt, $C^{10}H^{11}Ba''NO^3.SO^3.\frac{5}{2}H^2O$, and the mother-liquor dries up to an amorphous mass, consisting chiefly of the salt $C^{20}H^{24}Ba''N^2O^6.S^2O^6.5H^2O$. The acid $C^{10}H^{15}NSO^7$, or $C^{10}H^{13}NO^3.SH^2O^4$, separated from the latter salt by sulphuric acid, crystallises from absolute alcohol in large colourless square plates. Both the acids and their barium-salts react with ferric chloride like tyrosine-sulphuric acid, producing a splendid violet coloration.

RATOFFKITE. A granular or earthy blue variety of fluor-spar, mixed with clay, from Ratoffka in Russia.

RAUMITE. A mineral, apparently allied to esmarkite, from Raumo, in Finland, containing, according to Bonsdorff, 43·0 per cent. silica, 19·0 alumina, 19·2 ferric oxide, 12·55 magnesia, and 6·9 water. (Rammelsb. Mineralch. p. 836.)

RAZOMOFFSKIN. An argillaceous substance from Kosemuth in Silesia, containing, according to Gellner, 54·50 per cent. silica, 27·25 alumina, 2·00 lime, 0·37 magnesia, 0·25 ferric oxide, and 14·25 water (= 98·62).

REALGAR. Native protosulphide of arsenic, AsS (i. 386).

RECTIFICATION. The concentration of a volatile substance by distillation.

RED ANTIMONY. Native oxysulphide of antimony, or *Kermesite*, Sb^2OS^2 (iii. 446).

RED CHALK, or **REDDLE.** Earthy red hæmatite having a flat conchoïdal fracture; used as drawing chalk.

RED COPPER-ORE. Native cuprous oxide (ii. 70).

RED DYES. See DYEING (ii. 355).

RED HÆMATITE, or **RED IRON ORE.** Native anhydrous ferric oxide (iii. 337, 393).

RED IRON-VITRIOL, or *Botryogen*. Native ferroso-ferric sulphate from Fahlun (i. 651).

RED LEAD, or *Minium*. Red oxide of lead (iii. 551).

RED LEAD-ORE, or *Crocoïsite*. Native chromate of lead (i. 934).

RED MANGANESE, or *Diallogite*. Native carbonate of manganese (i. 789).

RED OCHRE. Red hæmatite of a soft earthy consistence. The same name is applied to a pigment prepared by calcining yellow ochre (clay containing ferric hydrate).

RED PIGMENTS. The red pigments most commonly used are red oxide of iron in various states, red oxide of lead, and vermillion. *Indian red* is pure red hæmatite finely ground. The same name is applied to a dark-red ferric silicate from the Persian Gulf, also used as a pigment. *Venetian red* and *colcothar* are coarser varieties of red hæmatite.—*Red ochre* (vid. sup.). *Bole of Armenia* is a red oxide of iron mixed with clay.—Respecting *red lead* or *minium*, see LEAD (iii. 551). A fine *red-brown* is obtained by mixing red lead with ferric oxide. *Vermillion* is mercuric sulphide prepared by sublimation (iii. 913). Native cinnabar is of a duller red colour. —*Antimony-vermillion*, a sulphide of antimony prepared by precipitating an antimony-salt with an alkaline hyposulphite, generally with hyposulphite of calcium, is a very solid red colour, little subject to change except by the action of strong alkalis. When triturated with drying oils, it acquires great vivacity and lustre, and forms an oil-colour well adapted for house and furniture painting (Hofmann's *Exhibition Report*, 1862, p. 79).—*Realgar*, or native red sulphide of arsenic, is also used as a red pigment.—*Mercuric iodide* affords a splendid scarlet, but it is very liable to change by the action of light.—*Cobalt-rose* is a fine rose-colour obtained by calcining nitrate of cobalt with magnesia.—*Arsenate of cobalt*, both the native variety and that which is prepared by calcining the arsenio-sulphide of cobalt in contact with the air, affords a very rich and permanent red colour; but it is very poisonous.—Various *red lakes* are prepared by precipitating infusions of madder, cochineal, and brazil-wood with solutions of alumina. (i. 656, 804; iii. 466, 750. See also *Chimie des Couleurs*, par J. Lefort, Paris, 1855, pp. 133—195.)

RED SILVER-ORE. See PROUSTITE (iv. 740), and PYRARGYRITE (iv. 753).

RED VITRIOL, or *Biberite.* Native cobalt-sulphate. (See SULPHATES.)

RED ZINC-ORE, or *Zincite.* Oxide of zinc containing manganese. (See ZINC.)

REDDLE. Syn. with RED CHALK.

REDRUTHITE, or *Copper-glance.* Native cuprous sulphide (i. 74).

REDUCTION. The abstraction of an electro-negative from, or addition of an electro-positive element to, any compound: thus an oxide deoxidised by the action of hydrogen, charcoal, &c., is said to be reduced: the addition of hydrogen to an organic compound, by the action of sodium-amalgam, &c., is also called an operation of reduction.

REFLECTION and **REFRACTION.** See LIGHT (iii. 608).

REGULUS. A metal reduced from its oxide or other compound by fusion with a reducing agent.

REISET'S SALTS. The diammonio- and tetrammonio- platinous salts, discovered by Reiset (iv. 673).

REISSACHERITE. A brown-black spring-deposit, occurring between slabs of gneiss at Wildbad-Gastein, and containing, according to Hornig, 34·15 per cent. manganic oxide, 14·16 ferric oxide, 7·59 calcic carbonate, 16·9 water, and 27·27 sand. (Rammelsb. Mineralch., p. 1008).

REMINGTONITE. Hydrated carbonate of cobalt, occurring as a rose-coloured incrustation at Finksburg, in Maryland (i. 782).

REMOLINITE. Syn. with ATACAMITE (i. 429).

RENSSELAËRITE. A mineral having the composition of talc, but the crystalline form of augite. It has a fine compact texture, is unctuous to the touch, translucent, and of a grey, whitish, greenish, brownish, or sometimes black colour. Hardness = 3·4. Specific gravity = 2·87. On account of its softness, translucency, and fine texture, it is worked in the lathe into inkstands and other forms. It occurs over large areas in Northern New York. Two specimens analysed by T. S. Hunt (Jahresb. 1858, p. 743), *a* from Grenville in Canada, *b* from Canton, New York, gave the following results:—

	SiO^2.	MgO.	FeO.	H^2O.		
a.	61·60	31·06	1·53	5·60	=	99·79
b.	61·10	31·63	1·62	5·60	=	99·95

RESIGALLUM. A term applied both to realgar and to orpiment.

RESINAPITIC ACID. A crystallisable acid resin obtained, together with other products, from the root of butter-bur (*Tussilago Petasites*). See TUSSILAGO.

RESINATES. A general name for the salts of the acids obtained from turpentine—viz., sylvic, pinic, and pimaric acid (*q.v.*). The general formulæ of these salts are $C^{20}H^{29}MO^2$ and $C^{40}H^{58}M''O^4$.

RESINEÏN, or **RESINONE.** This name is given by Frémy to a hydrocarbon (probably impure colophene, i. 1086) obtained by the dry distillation of colophony.

RESINS. A class of compounds of vegetable origin, characterised by being insoluble in water, mostly soluble in alcohol, uncrystallisable, and softening or melting at a moderate heat. They may be divided into—

1. Resins which *exude* spontaneously from plants, or from incisions in the stems and branches, and harden on exposure to the air. These are mostly mixtures, sometimes containing considerable quantities of gum or mucilage (*Gum-resins*), or of volatile oil (*Balsams*). They are for the most part produced by the oxidation of volatile oils secretd by the plant.

2. *Oxidised Fossil Resins*, occurring in beds of coal lignite, &c., and apparently produced in a similar manner from plants of a bygone age. The term fossil resin is sometimes, but inappropriately, extended to certain hydrocarbons, such as scheererite, ozokerite, &c., occurring in similar localities.

3. Resins *extracted* from plants by alcohol, and consisting in many cases of definite proximate principles.

Resinous bodies are also produced, artificially, by the oxidation of volatile oils in contact with air, or by the action of nitric acid; in the desiccation of drying oils; in the decomposition of alcohol, aldehyde, and similar compounds by potash, and in the dry distillation of many organic compounds.

Natural resins may be freed from admixed volatile oil by exposure to the air, by boiling with water, or by fusion; gummy or mucilaginous substances may be extracted from them by water.—When a resin has been extracted from a plant by hot alcohol or ether, the solution on cooling deposits the greater part of the wax or fat contained in it; and if it be then distilled with water, the resin remains behind, and may be further purified by washing with water.

The products thus obtained frequently retain small quantities of acid, fat, volatile oil, colouring-matter, &c., and may in some cases be resolved into two or more resins, differing in composition and properties.

Resins are transparent or translucent; a few are colourless, but the greater number are yellow, brown, or otherwise coloured. Some of them are hard and friable, a few are crystalline; others are soft and greasy, or elastic like caoutchouc. They become electric by friction. When heated they soften or melt, mostly without decomposition, to a thick tenacious liquid, generally more viscid than melted fat. They are not volatile, but when strongly heated, they carbonise, and give off carbonic anhydride, water, gaseous hydrocarbons, and volatile oils varying greatly in composition. (See COLOPHONY, i. 1087.)

Resins are insoluble in *water*; most of them dissolve freely in cold *alcohol*, some scarcely at all, or only in hot alcohol. The alcoholic solutions, when exposed to the air, give off the alcohol, and leave the resin in the form of a varnish. They are rendered milky by water, from separation of the resin; more complete separation is effected by mineral acids. Most resins are soluble in *ether*. *Volatile oils* likewise dissolve them, and the solutions, on exposure to the air, leave first a balsam-like mass, then the resin. Resins may be melted together with *fats*; their solutions in drying oils harden in contact with the air.

Resins are either *neutral* or *acid*. The former, when dissolved in alcohol, do not redden litmus, and they are insoluble or only sparingly soluble in *alkalis*. The latter, which are the more numerous, redden litmus in alcoholic solution, and dissolve in caustic alkalis and alkaline carbonates, the solutions, when evaporated, leaving amorphous masses, called resin-soaps, often precipitable from the solution by excess of alkali. Common yellow soap consists of tallow-soap mixed with a resin-soap, formed by dissolving colophony in caustic soda or carbonate of sodium. By decomposing the solutions of the resin-soaps with metallic salts, compounds of the acid resin with metallic oxides are formed, for the most part insoluble in water.

Resins are used for a variety of purposes. Their solutions in alcohol, oil of turpentine, and drying fat oils, yield the several kinds of varnish used for covering wood, metal, &c. with a thin but impermeable coating, in order to protect them from air and moisture. Spirit-varnishes are the most brilliant, but also the most brittle; their rigidity may be diminished by the addition of oil of turpentine. The resins commonly used for varnishes are copal, elemi, lac in scales, mastic, and sandarach.

The following is a list of the natural resins, showing, except in the case of the fossil resins, the plants from which they are derived:—

RESINS EXUDING FROM PLANTS.

a. Containing Benzoic or Cinnamic acid.

1. Acaroïd resin, from *Xanthorrhœa hastilis*.
2. Benzoïn, from *Styrax Benzoin*.
3. Dragon's-blood, Oriental, from *Calamus Draco*.

Dragon's-blood, Canarian, from *Dracæna Draco*.

Dragon's-blood, American, from *Pterocarpus Draco*.

α. *Containing Benzoic and Cinnamic Acid* (continued).

4. Peru Balsam, from *Myroxylon peruiferum*.
5. Liquid Storax, American, from *Liquidambar styraciflua*.
6. Liquid Storax, Oriental, from *Liquidambar Altingia*.
7. Solid Storax, from *Styrax officinalis*.
8. Tolu Balsam, from *Myrospermum toluiferum* or *frutescens*.
9. Mecca Balsam, from *Opobalsamum verum*, s. *gileadense*.

β. *Not containing Benzoic or Cinnamic Acid.*

1. Alouchi resin, from a tree growing in Madagascar.
2. Gum ammoniacum, from *Dorema ammoniacum*.
3. Anime resin, from *Hymenæa Courbaril*.
4. Arbol-a-Brea, from *Canarium album?*
5. Asafœtida, from *Ferula Asafœtida*.
6. Bdellium, from *Balsamodendron* (various species).
7. Betulin, from *Betula alba*.
8. Caranna, from *Amyris caranna*, *Bursera gummifera* or *acuminata*.
9. Ceradia resin, from *Ceradia furcata*.
10. Copaiba balsam, from various species of *Copaïfera*.
11. Copal, Brazilian or West Indian, from *Hymenæa Courbaril*.
    Copal, African and East Indian, from *Hymenæa verrucosa* or *Elæocarpus copaliferus*.
    Copal, North American, from *Rhus copallina*.
    Dammara resin, Australian, from *Dammara australis*.
    Dammara resin, East Indian, from *Pinus Dammara* or *Dammara alba*.
13. Elemi, from *Amyris* or *Icica* (various species).
14. Euphorbium, from *Euphorbia officinarum*, *antiquorum*, and *canariensis*.
15. Galbanum, from *Babon Galbanum?*
16. Gamboge, from *Stalagmites cambogioïdes* or *Hebradendron cochinchinense*.
17. Gomart resin, from *Bursera gummifera*.
18. Guaiacum, from *Guaiacum officinale*.
19. Icica-resin, from various species of *Icica*.
20. Ivy-resin, from *Hedera Helix*.
21. Jalap-resins, from *Convolvulus Schiedanus*, &c.
22. Labdanum or Ladanum, from *Cistus creticus*.
23. Lac, from *Aleurites laccifera*, *Croton aromaticus*, *Butea frondosa*, *Ficus religiosa*, and *Zizyphus Jujuba*.
24. Laëtia-resin, from *Laëtia resinosa*.
25. Masopin, from a Mexican tree.
26. Mastic, from *Pistacia Lentiscus*.
27. Maynas, from *Calophyllum Calaba*.
28. Myrrh, from *Balsamodendron Myrrha*.
29. Olibanum or Incense, Indian, from *Boswellia serrata*.
    Olibanum or Incense, Arabian, from *Amyris Kataf*.
30. Opoponax, from *Ferula Opoponax*.
31. Palm-wax (Cera de Palma), from *Ceroxylon andicola*.
32. Pasto-resin, from a Mexican tree.
33. Sagapenum, from *Ferula persica*.
34. Sandarach, from *Thuja articulata*.
35. Scammony, from *Convolvulus Scammonium* and other species.
36. Tacamahac, West Indian, from *Amyris tomentosa*.
    Tacamahac, East Indian, from *Calophyllum Inophyllum*.
37. Turpentine, from coniferous trees.

B. Fossil Resins (containing oxygen).—Amber, Ambrite, Anthracoxene, Asphalt, Berengelite, Boloretin, Bucaramanga-resin, Copalin, Euosmite, Fossil Caoutchouc, Guayaquillite, Hartin, Inolyte, Jaulingite, Krantzite, Melanchym, Middletonite, Peat-resins, Piauzite, Pyroretin, Retinasphalt, Retinite or Walchovite, Scleretinite, Resin from Settling Stones in Northumberland, Tasmannite, Xyloretin, Resins from the Lignite of Weissenfels—viz., Geoceraïn, Geoceric acid, Geocerinone, Geomyricin, Geoceric acid, Leucopetrin.

C. Resins extracted from Plants by Alcohol.

Nearly all plants yield resins when thus treated. Among them may be mentioned the resins of Angelica-root, Indian hemp, Cubebs, Manna, Poplar-buds, Butter-bur (*Tussilago Petasites*), Spanish pepper (capsicin), Squill (*Scilla maritima*), and Turpethum (*Ipomæa Turpethum*).

Most of the resins above enumerated have been or will be described in their alphabetical places. Some are not sufficiently important to require special description. We give here a few that have been omitted. (See further *Gmelin's Handbook*, xvii. 382—455):

1. *Gum Ammoniacum.*—This gum-resin exudes from an umbelliferous plant (*Dorema ammoniacum*, Don.; *Heracleum gummiferum*, Willd.) growing in the northern parts of Persia and Armenia. It occurs in commerce, sometimes in white, yellow, or reddish

grains of various sizes, sometimes in cakes mixed with sand and sawdust. It has a strong disagreeable odour, resembling that of garlic and of castoreum, and arising from the presence of an essential oil (probably sulphuretted), which may be separated by distillation with water. It softens at the heat of the hand, and becomes brittle when cooled. Specific gravity = 1·207. It contains, according to Bucholz, 72·0 per cent. resin, 22·4 soluble gum, 1·6 bassorin, and 4·0 volatile oil and water; according to Braconnot, 70·0 resin, 18·4 soluble gum, 4·4 bassorin, 7·2 volatile oil and water.

By digesting gum-ammoniacum with alcohol, a clear yellow solution is obtained, which yields by evaporation a transparent nearly colourless resin, containing, according to Johnston, 71·9 per cent. carbon, 7·6 hydrogen, and 20·5 oxygen. By heating this resin to 130 as long as it gives off vapour, another resin is obtained containing more carbon.

2. *Resin of Ceradia furcata.*—This plant, growing on the coast of Africa, opposite the island of Ichaboe, yields an amber-coloured resin, having the odour of olibanum, and a specific gravity of 1·197. It appears to have the composition of the turpentine resins, $C^{20}H^{30}O^2$.

3. *Gomart-resin*, from *Bursera gummifera.*—Solid, dry, rather soft in the middle, nearly white, and of crystalline structure, exhibiting cavities lined with shining crystals, slightly fusible; spreads out on boiling water in adhesive grains. The odour is intermediate between that of turpentine and that of elemi. Yields by distillation with water, a transparent colourless volatile oil, having the odour and composition of turpentine-oil, $C^{10}H^{16}$, vapour density = 4·7, and forming with hydrochloric acid gas a hydrochlorate, $C^{10}H^{16}.2HCl$, which crystallises in dazzling white silky needles.

4. *Ivy-resin*, from *Hedera Helix.*—Red-brown or greenish brittle lumps, having a specific gravity of 1·294 (Brisson). Has a faint aromatic taste and odour. Contains, according to Pelletier, 23 per cent. resin, 7 gum, 70 woody fibre, with malic acid and salts. It burns with a bright flame and agreeable odour; yields by dry distillation, first acid, then ammoniacal water, together with yellow and red oil.

5. *Resin of Laëtia resinosa.*—Small yellowish-white, transparent, green, brittle grains, with conchoïdal fracture. Has a faint aromatic odour. Yields a small quantity of volatile oil by distillation with water. When heated, it melts, swells up, burns with a white very smoky flame, leaving a bituminous cinder. Dissolves completely in boiling alcohol, and partly separates on cooling. (Macaire-Prinsep, Bibl. univ. xlv. 431.)

RESORCIN. $C^6H^6O^2$.—A compound homologous with orcin ($C^8H^{10}O^2$) produced by the action of potash on galbanum (iv. 215).

RESPIRATION. All animals, so far as we know, have need of oxygen in order that the oxidative processes, whereby their life is manifested, may be carried on. Some, the so-called air-breathing animals, obtain the oxygen they require from the atmosphere; others, the so-called aquatic animals, live on the free oxygen always to be found in those waters which are capable of supporting life. In order to bring the oxygen-bearing medium into close contact with the blood or internal juices of the body, a special mechanism is in most cases provided. Thus in man, by the alternate expansion and relaxation of the chest-walls, a quantity of air is alternately drawn into and driven out of hollow organs called lungs, situated in the chest, but having a direct connection with the external air; by means of bloodvessels ramifying over the lungs, the blood is brought very near to the air. Similar organs, with various modifications, are found in all the higher and in some of the lower air-breathing animals. In other cases, *e. g.* insects, air is carried by means of ramifying tubes all over the body. In many aquatic animals the blood or nutritive fluid is made to pass into or through organs called gills, so constructed that the water in which the animal is living is separated from the blood or nutritive fluid by a very thin membrane only. In others water is carried by canals (water-vascular organs), by a system of irrigation as it were, through a smaller or larger portion of the body. Finally, all animals are capable, to a greater or less extent, of acting upon and being acted upon by the surrounding oxygen-bearing medium, be it air or water, through the external surface of their bodies and through the walls of various cavities (digestive, &c.). In many of the lower animals this is the only way in which oxygenation takes place, no special organ of any kind being provided for that purpose.

The word breathing or respiration was at first used to denote the visible play of the mechanism, whereby the oxygen-bearing medium was brought near to the fluids of the economy,—namely, the driving air into (inspiration) and out of the lungs (expiration), or analogous functions, in other animals,—and is still often employed in this limited sense. Inasmuch, however, as a particular respiratory mechanism is not essential to the gaining of oxygen, while the gaining of oxygen is the end of every respiratory mechanism, it has become a habit to consider respiration to mean the absorption of free oxygen by any means whatsoever. And since it so happens that at the same time and place, and by the same organs that oxygen is taken into the economy, carbonic acid is also given out from it, and other changes of gases possibly take place, the term has acquired the still wider signification of "the interchange between the gases of an organism, and the gases of the medium in which it lives."

Theory of Respiration.

The ancients were for the most part agreed that the great use of breathing was to cool the lungs and moderate the heat generated in the viscera; and this opinion maintained its ground, to a great extent, through the middle ages into modern times, in spite of the anatomical and physiological labours of Vesalius and Harvey. The observations of Van Helmont (1648), on the unfitness of *gas sylvestre* for breathing purposes; of Boyle (1670), on the necessity of air for the respiration, not only of all terrestrial but also of aquatic creatures, and on the unfitness of respired air for further respiration; of Hook (1664) on artificial respiration; and of Lower (1669), on the change of colour to be observed in blood while passing through the lungs, prepared the way for the striking views of John Mayow (1674). This young physiologist recognised, as a constituent of atmospheric air, of nitre, and of other substances, and as a necessary factor of combustion, a something which he calls *spiritus nitroaëreus* or *particulæ nitroaëreæ sive igneoaëreæ*, and by which he evidently meant what we now call oxygen. He observed that by respiration, as by combustion, air was deprived of its *particulæ nitroaëreæ*; and he was the first to remark that when animals were made to breathe in a limited space, as in a bell-jar over mercury, the volume of the air was lessened. He maintained that the use of respiration was not to cool the blood, or to promote the transit of that fluid through the lungs, or to encourage a due mixture of its component parts, but to supply it with the *particulæ nitroaëreæ*; and he was of opinion that these particulæ, embraced by the blood and carried by it to the muscles, entered into such a violent molecular conflict with the combustible or (as he calls it) sulphureous material there stored up, as to produce the phenomena of muscular contraction. With these views Mayow mixed up many crude and immature ideas, from which, had he lived longer (he died A.D. 1679, æt. 33) he might have freed himself. His great lack was the failing to recognise that in respiration (and combustion) there was something produced as well as consumed. This, however, was not fully shown until Black (1757) demonstrated the existence of carbonic acid in expired air. The next step was made by Priestley, who showed (1771) that air which had become unfit for respiration or combustion, by reason of animals having breathed, or candles having burnt, or substances having putrefied in it, regained its lost properties on being submitted to the influence of living plants (*On Air*, 2nd ed. 1775). He marred the good of his discovery by adopting a retrograde theory of the nature of respiration and combustion. He maintained that the carbonic acid (fixed air) of expired air did not come from the lungs, but pre-existed in common atmospheric air, and was "precipitated" therefrom by the union of the air of inspiration with the phlogiston (ultimately derived from the food) which was thrown off by the lungs. Living animals (and burning or putrefying bodies) phlogisticated, he said, and living plants dephlogisticated common air. Priestley, however, prepared the overthrow of his own views by the discovery of oxygen (1774–5). Through experiments made in 1777, but not published till 1779, Crawford (*Animal Heat*, 2nd ed. 1788) was led to connect animal heat with respiration. He says (p. 361): "The pure air is received into the lungs containing a great quantity of elementary fire; the blood is returned from the extremities impregnated with the inflammable principle; the attraction of pure air to the latter principle is greater than that of the blood. This principle will therefore leave the blood to combine with the air; by this combination the air is obliged to deposit a part of its elementary fire; and as the capacity of the blood is at the same moment increased, it will instantly absorb that portion of fire which had been detached from the air. The arterial blood, in its passage through the capillary vessels, is again impregnated with the inflammable principle, in consequence of which its capacity for heat is diminished. It will therefore, in the course of the circulation, gradually give out the heat which it had received in the lungs, and diffuse it over the whole system. Thus, in respiration, the blood is continually discharging the inflammable principle, and absorbing heat, and in the course of the circulation is continually imbibing this principle and emitting heat."

Meanwhile the true theory of respiration had been more clearly and distinctly propounded by Lavoisier, who, following up his investigations on oxidation and on the constitution of air, in 1777 (*Expériences sur la Respiration des animaux et sur les changements qui arrivent à l'air en passant par leur poumon*, Mémoire lue à l'Académie des Sciences le 3 Mai 1777, Œuvres, éd. imp. 174), demonstrated that animals by the act of breathing took away from the atmosphere oxygen (*l'air éminement respirable*), and loaded it with carbonic acid (*l'acide crayeux aëriforme*). He hesitated to decide whether the oxygen was converted into carbonic acid while passing in and out of the lungs, or whether oxygen was absorbed into, and carbonic acid exhaled from, the blood during its passage through the lungs; but inclined to the former opinion. In 1780 he showed, in conjunction with La Place (Mémoire sur la Chaleur, Art. iv., Œuvres, éd. imp. ii. 283), that by far the larger portion of the heat given out by animals during a given period could be accounted for by considering it to be due to the combustion of a quantity of carbon sufficient to produce the carbonic acid exhaled during the same time. In 1785 (*Altérations qu'éprouve l'air respiré*, Œuvres, éd. imp. ii. 676), he recognised that the whole of the oxygen which disappeared during respiration, did not return in the form of carbonic acid; and while admitting the possibility of the missing portion having "combined with the blood," thought it more probable that it united with hydrogen in the lungs to form water. He had by this time definitively adopted the theory that the formation of carbonic acid took place in the lungs, and in a memoir published in 1790 (*Premier Mémoire sur la Transpiration des Animaux*, par Séquin et Lavoisier, Œuvres, éd. imp. ii. 708), he gives the following account of his views on the subject. There is continually transuding from the blood through the pulmonary membranes into the air-tubes, a humour which is principally composed of carbon and hydrogen. This humour, issuing from the minute exhalant vessels of the lungs in a state of very fine division, unites with the oxygen in contact with it, and is thus converted into water and carbonic acid. The carbonic acid is driven out by the action of the lungs while the accompanying water (water of respiration), together with the water which transudes into the air-tubes along with the hydrocarbonous respiratory material (water of pulmonary transpiration) is carried off in the form of vapour by the heated air of the lungs.

The difficulty felt in supposing that, while the whole body is nearly of the same temperature, combustion takes place in one spot only, to wit the lungs, was met by Lavoisier and La Place with the reflection that the rapidity of the circulation, the evaporation by the lungs, and an augmentation of the capacity for heat in decarbonised blood (theory of Crawford), were sufficient to account for the phenomena. Lagrange however, dissatisfied with this explanation, put forward through Hassenfratz the theory (which Lavoisier had discarded) that oxygen was absorbed into the blood, and, during the course of the circulation, combined with the carbon and hydrogen of that fluid, giving rise to carbonic acid and water, which were in turn exhaled through the lungs. Lagrange supported his views by no facts or experiments, and they did not meet with any general acceptance.

In 1799 H. Davy (Beddoe's Med. Contrib. p. 128) published a theory that in the act of respiration, phosoxygen, as he called it, combined with venous blood, while at the same time "carbonic acid and water were liberated, either by the increase of temperature, or from the superior affinity of phosoxygen for venous blood." He was able to obtain a small quantity of carbonic acid from venous, and a very small quantity of oxygen from arterial blood. In 1800, however (*Researches*, p. 447), he had abandoned his phosoxygen theory, and embraced the views of Lavoisier, though he was led, by his experiments on the respiration of hydrogen and nitrous oxide, to believe that some at least of the carbonic acid of expired air did not arise directly from a combustion of carbon in the lungs, but pre-existed in venous blood, and transpired from it through the coats of the minute bloodvessels.

Spallanzani (*Memoirs on Respiration*, by Sennebier) in the course of some experiments which were not published until 1803, found that snails placed in an atmosphere of pure hydrogen, still continued for some time to give off carbonic acid, which in this case could not have arisen from any direct combustion of carbon. Singularly enough, he explained this fact by supposing that carbonic acid was generated by the food in the stomach, entered thence into the blood, and so made its way through the skin and lungs.

These observations of Davy and Spallanzani were overlooked by physiologists, until W. F. Edwards (*Influence of Physical Agents on Life*, by Hodgkin, p. 226), showed in 1823 that frogs, fish, and infant mammalia, when placed in an atmosphere of hydrogen, exhaled a quantity of carbonic acid, far too great to be accounted for by the consumption of the small amount of oxygen still remaining in the lungs of the animals at the moment of their being removed from atmospheric air.

About this time, and for some years afterwards, there may be said to have been three main theories of respiration adopted or discussed by physiologists. There was the theory of Lavoisier, either in the actual form in which he enunciated it, or that modification of it which was more generally received in England—viz., that the hydrocarbonous material which suffered combustion in the lungs was not secreted as such into the air-vesicles, but was oxidised while still in the venous blood by means of the passage of air or oxygen through the coats of the bloodvessels. This, which might be called the "combustion" theory, obtained by far the greatest amount of support, and indeed may still be found in books of the present day. Another opinion was that either air as a whole, or the oxygen of it only, passed through the coats of the blood-vessels and combined with the blood, while at the same time the lungs, out of the hydrocarbonous material with which venous blood was supposed to be loaded, developed or secreted carbonic acid. This "secretion" theory, constructed chiefly to explain the results of Edwards, corroborated as they were by those of Collard de Martigny, Bergmann, Müller, &c., was embraced by a few only. It is somewhat strange that the tendencies of the present day seem nevertheless to be turning back to a modification of this view. Lastly, there was the old suggestion of Lagrange, that oxygen passing by solution into the blood was consumed in the capillaries, giving rise to carbonic acid, which escaped by the lungs. This "diffusion" theory was mostly rejected by reason of the difficulty that was met with in attempting to demonstrate the existence of free carbonic acid in venous or of free oxygen in arterial blood. Thus while H. Davy, Nasse, Vogel, Brande, Home, Scudamore, Collard de Martigny, Maitland, Vauquelin, Stevens, Hofman, Entschut, and Bischof obtained, either by heat or the vacuum, or by a current of some indifferent gas, evidence of the existence of free carbonic acid in venous blood, J. Davy, Strohmeyer, Bergmann, J. Müller, and Tiedemann with Gmelin and Mitscherlich, failed to do so; and while H. Davy obtained a small quantity of oxygen from arterial blood, subsequent observers were unsuccessful. The "combustion" theory therefore, in consequence of this discordance, retained its hold upon physiologists until the experiments of Magnus in 1837, who made an epoch in this subject by definitely determining the gases of blood.

In his first researches (Pogg. Ann. xl. p. 583) Magnus repeated the experiments of his predecessors, who attempted to drive off from blood its free carbonic acid by means of a stream of hydrogen. By continuing the current for 24 hours, he obtained as much as 34 cc. of carbonic acid from 62·9 cc. of blood. Subsequently, on observing that in using the air-pump blood could not be made to give up its gases until a very great exhaustion had been arrived at, he constructed a mercurial air-pump, and by this means was enabled to demonstrate the existence in both arterial and venous blood of very considerable quantities of oxygen, nitrogen, and carbonic acid:—

	Quantity of blood used.	Total quantity of gas.	CO^2.	O.	N.
Horse: artery . . .	125 cc.	9·8 cc.	5·4 cc.	1·0 cc.	2·5 cc.
" vein . . .	205	12·2	8·8	2·3	1·1
" " . . .	195	14·2	10·0	2·5	1·7
Very old Horse: artery .	130	16·3	10·7	4·1	1·5
" " " .	122	10·2	7·0	2·2	1·0
" " vein .	170	18·9	12·4	2·4	4·0
Calf: artery . . .	123	14·5	9·4	3·5	1·6

Hence, while both kinds of blood alike contain oxygen and carbonic acid, arterial blood contains more oxygen and less carbonic acid than does venous blood. Although the quantities of these gases thus obtained could not be supposed to represent all the gas really present in a free state in the blood, Magnus satisfied himself that the amount of carbonic acid determined by his experiments was sufficient to account for the whole quantity given off by the body in health. Further experiments (Poggend. Ann. lxvi. p. 177, 1845) taught him that blood shaken up in an atmosphere of oxygen will absorb from 10 to 12 per cent. (of volume) of that gas, a quantity sufficient to account for all the oxygen consumed by the economy. He was thus led to adopt in its entirety the "diffusion" theory; and the demonstration of the existence of free gases in the blood having been the one thing lacking to this theory, he was in this followed by nearly all physiologists. He regarded the gases as simply dissolved in the blood, and explained the entrance of oxygen and the exit of carbonic acid by a reference to the Henry-Dalton law of pressures (see GASES, ABSORPTION OF, BY LIQUIDS). According to this view, which was more fully elaborated by Vierordt (*Physiologie des Athmens*), the carbonic acid neither replaces nor is replaced by the oxygen, but both are taken up and given off independently of each other. (The idea of Valentin and Brunner, that the phenomena of respiration form an example of Graham's law of transpiration of gases, was shown by Regnault and Reiset to be erroneous; these observers having proved that in the animal economy the ratio between the amount of oxygen absorbed and that of the carbonic acid exhaled is not constant). The venous blood laden with carbonic acid, on being exposed, during the passage through the lungs, to an atmosphere containing but little of that gas, must, in obedience to the law of pressures, give off a portion of its carbonic acid, and will continue to do so until an equilibrium is established between the tension of the carbonic acid in the air of the lungs, and the tension of carbonic acid in the blood. Similarly venous blood, poor in oxygen, on being exposed to the air of the lungs, will absorb oxygen until an equilibrium is established between the tension of oxygen in the air of the lungs, and the tension of oxygen in the blood. And inverse processes will take place in the systemic capillaries between the arterial blood and the tissues. In each case the exact point at which equilibrium is established will depend on the so-called "absorption-coefficient" of blood for oxygen and carbonic acid respectively.

Before long, however, it began to be seen that this view was open to many objections. Liebig, in his *Chemical Letters* (by Gregory, 3rd ed. p. 332), strongly advocated the opinion that the condition of the greater part of the oxygen in the blood was one not of simple physical absorption, but of chemical combination—a combination, however, so loose that it was capable of being disturbed by the action of indifferent gases or of the vacuum. In support of his view, he drew attention to an analogous combination between carbonic acid and aqueous solutions of phosphate of sodium, cited the experiments of Regnault and Reiset, which showed that in an atmosphere of pure oxygen, animals consumed the same amount of that gas as when breathing ordinary air, and instanced the fact that in high regions, where the absolute quantity of oxygen taken into the chest at a breath is only about two-thirds of that taken in at the sea-level, the vital processes do not suffer any marked changes, such as would certainly follow variations in the quantity of oxygen absorbed. He, moreover, pointed out the necessity for accurately determining the absorption-coefficients of blood for its gases. This was afterwards attempted by Lothar Meyer, Fernet, and others, whose investigations, while they may be considered to have explained the entrance of oxygen into the blood, have left the question of the exit of carbonic acid still somewhat unsettled.

Absorption of Oxygen.

L. Meyer (for whose figures see vol. i. p. 606, vol. ii. p. 803) found that when blood was exposed to oxygen at various pressures, the quantity of that gas taken up might be regarded as consisting of two portions, one following the law of pressures, the other wholly independent of pressure. The former however, in respect to which blood differed very little from water, was found to be so small compared with the latter that the increments of absorption due to increments of pressure were almost covered by errors of observation. He accordingly drew the conclusion that oxygen was chemically combined with the blood during the passage through the lungs, though in *so loose* a fashion that it could be driven off again by the action of indifferent gases, or of the vacuum assisted by heat. Fernet (Ann. Sc. Nat. [iv.] viii. p. 125) arrived at the same conclusion, and moreover pointed out that this special affinity for oxygen was possessed not by the serum or plasma, but by the red corpuscles. Thus the proper absorption-coefficient of blood for oxygen was found to be ·0288 at 16°, of serum ·0288 at 16·8° (the absorption-coefficient of water at 16° for oxygen being ·02949); while 1 vol. blood chemically combined with ·0958 vol., and 1 vol. serum with ·00117 vol. oxygen at the same temperature. Neither Meyer nor Fernet, however, were able to obtain from arterial blood, by means of the vacuum, as much oxygen as was absorbed by venous blood when agitated in an atmosphere of that gas. But this difficulty was removed by Setschenow (Wien. Akad: Ber: xxxvi. p. 293), who, using a much larger vacuum, was enabled to drive off from blood much larger quantities of oxygen (see table below). The affinity for oxygen possessed by blood was also shown by the experiments of W. Müller (Ann. Ch. Pharm. cviii. p. 257), who found that animals (rabbits), made to breathe a limited amount of oxygen, consumed the whole of it, provided that the quantity placed at their disposal did not exceed 150—200 cc. The same observer ascertained that the residual air in lungs of asphyxiated animals contained a trace only of oxygen, a fact which was corroborated by Setschenow, and is directly opposed to the theory that the absorption of oxygen takes place according to pressure.

The behaviour of blood towards carbonic oxide has been found to illustrate the chemical nature of the process of absorption (Bernard, Leçons, Subst. Toxiq. 1857, p. 157; L. Meyer; Hoppe, Virch. Arch. xi. 288). Blood, when agitated with or treated with a stream of carbonic oxide, becomes of a peculiar bright red colour, and is found, not only to have given off its oxygen, but to have become incapable of absorbing that gas. It has lost the property of becoming arterialised. There is reason to believe that carbonic oxide has a stronger affinity than oxygen for the hæmoglobin or red colouring-matter of the blood, and forms with it a more stable compound (see below). Nawrocki (Henle u. Meissner, 1863, p. 298) finds that the amount of oxygen driven off by a stream of carbonic oxide tallies extremely well with that obtained by means of the mercurial vacuum, and it has been adopted by some subsequent observers (Bernard, Estor et Saintpierre) as a method of estimating the amount of oxygen in blood.

A still further advance has been made by the optical studies of Hoppe-Seyler (Virch. Arch. xxxiii. 446, xxix. 233 and 597; Med. Centralbl. 1864, p. 817; Handb. Chem. Anal. p. 201) and Stokes (Proc. Roy. Soc. xiii. 355). The red corpuscles of vertebrate animals consist for the most part of a substance which has been called *hæmatocrystallin* or *hæmatoglobulin*, or shorter *hæmoglobin* (Hoppe) or *cruorin* (Stokes), and which may often be obtained in a crystalline form. When tolerably concentrated solutions of this body, which are found to contain free oxygen and are of a blood-red colour, are examined with the spectroscope (or simply with a prism and slit in Stokes' way) there is found to be little absorption of light in that part of the spectrum which reaches from the extreme red to ¾ths of the distance between C and D, while in the remaining ¼th the absorption is much stronger. When the oxygen has been driven out of the solution by a current of hydrogen or carbonic acid, there is witnessed a very great increase of absorption of light at the red end, except in the space between *a* and B, and even in this part there is a slight increase of absorption. Upon these optical properties probably depends the difference in colour between arterial and venous blood. Venous blood viewed by the spectroscope without exposure to air, shows a very distinct absorption of light from B to beyond C, an effect which disappears when the blood is oxygenated by agitation with air. (Hoppe.)

Dilute solutions of blood-colouring-matter show two very dark and sharply-defined absorption-bands (visible in a 1 cc. thick layer of a solution of 1 grm. of colouring-matter in 10,000 cc. of water) between D and E, one being close to D, the other and thicker one being close to E; if D is at 80 of the scale and E at 106, the first band reaches from 81 to 87, the second from 95 to 106 (Hoppe, Stokes). When such a solution is treated with any reducing agent, such as a solution of ferrous sulphate or stannous chloride with tartaric acid and ammonia, it assumes a purplish colour, loses the two distinct bands, but gains a new one reaching from 82 to 97, with fainter bands extending on either side from 77 to 82 and from 97 to 99. If the solution be now agitated with air, it becomes blood-red again, and exchanges the new band for the two original ones (Stokes, Hoppe). The same effects may be produced by using sulphide of ammonium as a reducing agent, or by passing a stream of carbonic acid, hydrogen, nitrogen, &c. through the solution, or by keeping the solution for some little time at a blood-heat, or for a longer time at the ordinary temperature. In all these cases, the two original bands are found to be replaced by an intermediate band, and may be brought back again by agitating the solution with air or oxygen, the phenomena being accompanied by a change of colour from scarlet to purple and *vice versâ*. Hence the conclusion has been come to that there is a substance, holding oxygen in loose combination, giving two absorption-bands, and possessing a scarlet hue—the *scarlet cruorin* of Stokes, the *oxyhæmoglobin* of Hoppe; this body may give off its loose oxygen, either to some reducing agent or to some of its fellow blood-constituents (or to the tissues), and then has a purple hue and shows only one marked band—the *purple cruorin* of Stokes, the *hæmoglobin* of Hoppe; on exposure to air or oxygen, the purple cruorine or hæmoglobin absorbs oxygen, and becomes once more the scarlet cruorin or oxyhæmoglobin. And it is presumed that this is the way in which the red corpuscles of blood perform their share in the work of respiration. The hæmoglobin or purple cruorin of the blood of the pulmonary artery, absorbing oxygen, becomes oxyhæmoglobin or scarlet cruorin, and in the course of the circulation gives up its oxygen, becoming mere hæmoglobin or purple cruorin. Since venous blood always contains some oxygen, one must expect to find the spectrum of oxyhæmoglobin even in venous blood examined without any exposure to air, and such is the case (Stokes, Hoppe). The blood of an animal dying of asphyxia, however, contains no oxygen, and shows very distinctly the band of hæmoglobin or purple cruorin alone. (Hoppe.)

When a solution of oxyhæmoglobin is treated with carbonic oxide, oxygen is set free; the carbonic oxide, however, does not act as a reducing agent, the blood does not become purple from the formation of hæmoglobin, but of a peculiar bright red colour from the combination of carbonic oxide with hæmoglobin, to form carboxydhæmoglobin, whose spectrum is similar to that of oxyhæmoglobin, there being only a slight difference in the position of the bands—one reaching from 82 to 90, the other from 95 to 106 (Hoppe). The combination between carbonic oxide and hæmoglobin is not (or at least only slowly and partially) decomposed by exposure to air or oxygen. The carbonic oxide may, however, be replaced by nitric oxide, the blood being scarcely changed in colour, remaining still a bright red, and the spectrum resembling that of oxyhæmoglobin, but with bands less strongly marked. Nitric oxide may also be directly combined with hæmoglobin, and also with oxyhæmoglobin; in the latter case some nitric oxide is oxidised at the expense of the loose oxygen. A given quantity of hæmoglobin unites with equal *volumes* of oxygen, carbonic oxide, and nitric oxide (Hermann, L. Arch. Anat. Phys. 1865, p. 469). It is calculated that 1 grm. hæmoglobin unites with 1·3 cc. of gas.

The entrance of oxygen into the economy being therefore in the main not a physical process of absorption, but a chemical one of oxidation (and reduction) the amount of the oxygen in the inspired air, provided only there is enough for ordinary purposes, will have little or no effect on the amount of oxygen taken into the blood. We accordingly find that animals consume the same amount of oxygen and produce the same amount of carbonic acid when breathing pure oxygen as when breathing ordinary air (Regnault and Reiset). Nevertheless, many observers have from time to time described as effects of breathing pure oxygen, symptoms which have been interpreted as indicative of increased oxidation, which can hardly be considered as due to an augmentation of that fraction of oxygen which is really physically absorbed, and which have not been otherwise clearly explained.

Exhalation of Carbonic Acid.

L. Meyer (*op. cit.*), by exposing blood to carbonic acid at various pressures, found that the quantity of that gas absorbed might be divided into two portions, one obedient to and the other independent of the law of pressures. The absorption of carbonic acid differed notably from that of oxygen, inasmuch as the portion following the law of pressures was much larger than that which was independent. Thus at 11°—12° the former per vol. blood was, measured at 0° and ·76 met., 1·151, the latter ·630. Since blood contains carbonate and phosphate of sodium, and since aqueous solutions of these salts possess the power of holding, in loose combination, a quantity of carbonic acid over and above that due to simple physical absorption, it had been suggested that the absorption of carbonic acid by blood might bear some relation to these saline constituents. Fernet accordingly (*op. cit.*) studied the behaviour towards carbonic acid of aqueous solutions of these salts, taking the average composition of blood as a standard. He found that on the one hand they absorbed a quantity of carbonic acid according to the law of pressures (and in this respect possessed absorption-coefficients differing very slightly from that of water); while on the other hand the solution of carbonate of sodium absorbed, independently of pressure, a quantity of carbonic acid sufficient to convert the simple carbonate into bicarbonate, and the solution of phosphate of sodium similarly absorbed a quantity at the rate of two equivalents of carbonic acid to each equivalent of the salt. (According to recent researches of Heidenhain and Meyer, Stud. Bresl. ii. 103, Fernet's results require some corrections). He moreover found that blood behaved in respect to the absorption of carbonic acid almost exactly as if it were a mere aqueous solution of the saline constituents in their proper proportions; neither the corpuscles nor the organic substances of the serum had any marked share in the matter.

By submitting blood to the action of a vacuum and moderate heat, Meyer obtained only small quantities of carbonic acid; by far the greater part of the total amount contained in the blood could not be driven off unless acids were employed. Setschenow, however (*op. cit.*), by the help of his larger vacuum, gained much larger quantities without using any acids. His results, together with those of some subsequent observers, are given in the following table, where "loose" carbonic acid means that which is given off to a vacuum, and comprises both that which is physically absorbed, and that which is retained by the carbonate and phosphate of sodium, while "fixed" means that which is driven off by the use of acids:—

Gases (measured at 0° 1ʹ) in 100 vols. Blood.

	O.	N.	Loose CO^2.	Fixed CO^2.	Total CO^2.	
Carotid: Dog .	15·05	1·192	30·66	2·54	33·20	Setschenow.
" " .	16·41	1·20	28·27	2·32	30·59	
Venous " .	4·10	·78	. .	. .	35·21	
Asphyxia " .	1·161	4·728	33·168	4·366	37·534	
" " .	trace	1·399	28·012	3·286	31·298	
" " .	"	1·184	38·152	4·011	42·163	
" " .	"	1·955	38·857	1·791	40·648	
Artery " .	16·289	·931	27·216	1·173	28·389	Sczelskow.
Vein " .	8·217	·951	32·159	2·102	34·261	
Artery: Dog .	11·39	4·18	30·88	1·90	32·70	Schöffer.
Vein " .	4·15	3·05	29·82	5·49	35·31	
Artery . .	. .	. .	29·45	2·92	32·37	
Vein . .	. .	. .	34·26	3·81	38·07	
Artery . .	17·70	1·25	31·65	trace	. .	
Vein . .	9·20	1·00	33·05	3·05	36·10	
Artery .	15·24	1·23	26·44	trace	. .	
Vein . .	12·61	1·17	27·83	1·67	29.50	
Artery . .	11·76	1·66	28·02	1·26	29·28	
Vein . .	8·85	1·25	32·53	3·06	35·59	
Artery . .	16·95	1·80	26·80	0·67	27·47	
Vein . .	10·46	1·15	30·26	1·57	31·83	

The recent observations of Plüger (*Ueb. d. Kohlensäure d. Blutes*) seem to invalidate these results. This observer, by using a vacuum free from aqueous vapour, was enabled to drive off the whole of the carbonic acid, so that no more could be obtained by the addition of acids; even neutral carbonate of sodium previously added to the blood was decomposed. It is probable that this result was brought about, in part at least, by acids arising from the decomposition of the hæmoglobin; and, though a portion of the carbonic acid was obtained much more readily than the rest, the experiments suggest the question whether generation of acids does not take place in all cases where the vacuum is used—whether, in fact, the above distinction between loose and fixed carbonic acid is not in great measure a factitious one.

That the escape of carbonic acid is, taken as a whole, a matter of pressures is shown by the results of all observers; but there are considerable difficulties connected with the subject, which have not as yet been thoroughly cleared up. Were the venous blood, during its passage through the lungs, exposed to air containing little or no carbonic acid, the law of pressures would readily suggest a cause for the immediate escape of the due amount of that gas. Such, however, is not the case. We are led to believe (Becher) that the air in the pulmonary air-cells contains habitually about 8 per cent. of carbonic acid. Hence, any just explanation of the process of exhalation must take into account the existence to that extent of a tension of carbonic acid in the lung-air, which has to be overcome before any escape can take place from the blood. Thus the hypothesis that in the lungs the acid carbonate of sodium is reduced, by mere exposure to lung-air, to the neutral carbonate, with escape of carbonic acid, is untenable, because the acid carbonate refuses to give up its extra atom of carbonic acid to air containing above 1 per cent. of that gas (Meyer). Similarly the carbonic acid retained by a solution of phosphate of sodium is not given off to an atmosphere of like carbonic acid tension (Schöffer, Wien. Akad. Ber. xli. p. 589). Holmgren (*loc. cit.*, xlviii.) has attempted to determine the actual degree of tension of carbonic acid which a vacuum (containing aqueous vapour) must acquire before blood ceases to give off to it its carbonic acid. This he found to be, at 40° C., 22·3 mm. of mercury for arterial blood, 30·6 mm. for venous blood, and 38·1 mm. for the blood of asphyxia. In two cases, where the normal expired air contained respectively 2·94 per cent. and 4·31 per cent. of carbonic acid, and therefore gave tensions of 22·18 mm. and 31·98 mm., the blood ceased to give off carbonic acid at the tensions of 22·13 and 28·20 mm. Since the carbonic acid tension of the interior lung-air is much higher than that of the expired air, it is obvious that in these cases the blood could not have got rid of its carbonic acid while passing through the lungs, through the simple working of the law of pressures, unless there were something at hand in the lungs temporarily augmenting the carbonic acid tension of the blood, or otherwise assisting the escape of that gas. This is still more strikingly shown in two cases of asphyxia, where the tension of the blood was 34·76 and 41·41, of the lung-air 98 and 91·6 mm. respectively. Holmgren further observed that blood gave up its carbonic acid more readily to a rarefied atmosphere of oxygen than to a vacuum containing nothing but aqueous vapour. Thus 153 cc. of blood gave up to a vacuum of 150 cc. at 22°, 0·418 cc. and 0·583 cc. of carbonic acid (measured at 0° 1′), while to the same space containing 8·99 cc. and 20·16 cc. oxygen, there were given up 1·375 cc. and 1·997 cc. of carbonic acid by the same quantities of the same blood. These results suggest the idea that the act of the absorption of oxygen in some way or other momentarily augments the tension of carbonic acid in the blood. But in what way is it able to produce such an effect? It has been shown that a certain portion of the carbonic acid of the blood is given off more readily than the rest, and it has been also shown that this fixed or stable remainder is greater in venous than in arterial blood (vide table, *ante*). In other words, during the passage through the lungs, a certain portion of the fixed or stable carbonic acid becomes unstable or loose, and it has been maintained by Schöffer (*op. cit.*) that the amount thus converted is sufficient to account for the quantity escaping into the air. Now Preyer (Wien. Akad. Ber. xlix.) has shown that the same conversion of stable into unstable carbonic acid takes place when venous blood is artificially arterialised by agitation with air or oxygen, whereas the amount of stable carbonic acid existing in serum is wholly unaffected by any such treatment. Hence it has been supposed that oxygen in the act of combining with hæmoglobin effects in some way or other (by the development of an acid?) some kind of decomposition, whereby a certain amount of fixed or stable carbonic acid is converted into loose carbonic acid, the tension of carbonic acid in the blood proportionately augmented, and the escape of that gas into the air thus brought about: or, disregarding the distinction between loose and fixed, we may say that the absorption of oxygen is attended with a liberation of carbonic acid within the blood, leading to an increase in the tension of the gas, and its consequent escape.

Absorption and Exhalation of Nitrogen.

The quantity of nitrogen in blood is very small, and the observations with regard to its being absorbed or exhaled by the lungs have been remarkably discordant. Fernet (*op. cit.*) found the absorption-coefficient of serum for nitrogen to be nearly exactly that of an aqueous solution of its saline constituents in their proper proportions, that is to say, a little less than that of water (at 15° 3′ serum, ·0141, at 15° water ·01478). Setschenow (*op. cit.*), on the other hand, obtained for blood as a whole a higher absorption-coefficient than that of water, and therefore concluded that the blood-corpuscles are able chemically to combine with a small quantity of nitrogen.

Qualities of Respiratory Oxygen.

Schönbein and His remarked that the red corpuscles of the blood acted like finely-divided platinum, &c., upon a mixture of tincture of guaiacum with peroxide of hydrogen, ozonised turpentine, ether, &c., in producing a deep blue colour. Various animal substances possess this property in a greater or less degree, but none approach the red corpuscles, or rather the colouring-matter of the red corpuscles, in intensity of effect. The presence of red corpuscles also vastly augments the rapidity with which a solution of indigo is decolorised and hydriodic acid decomposed by peroxide of hydrogen, ozonised turpentine, &c. These observers were unable to produce any oxidative action on guaiacum with blood, unless one of the so-called ozone-bearers were present. A. Schmidt (*Ueber Ozon im Blute*, 1862), however, has shown that, under certain precautions, blood by itself will turn guaiacum blue. If a strip of paper be dipped in tincture of guaiacum (1 pt. gum to 6 of 80 per cent. alcohol) and dried, a drop of dilute blood or of dilute solution of hæmoglobin placed on it will give an intense blue ring. No other substance in the animal body is able to produce this effect. A similar process of oxidation may with care be witnessed when hydriodic acid or an indigo solution is treated with blood. Blood, or a solution of hæmoglobin, will also decompose peroxide of hydrogen with an energetic evolution of oxygen; and will decompose sulphydric acid with precipitation of sulphur. According to the ozone theory, therefore, oxygen in combination with hæmoglobin is that form or kind which is called ozone. The oxygen, however, which is driven off from blood by the passage of a stream of other gases, gives none of the reactions of ozone, and blood entirely deprived of its oxygen by carbonic oxide still gives the reaction with guaiacum; this reaction, however, ceases to be manifested when the experiment is conducted with total exclusion of atmospheric air. Hæmoglobin therefore, in addition to its power of absorbing oxygen and of transferring it in an active state to other bodies, is able, like finely-divided platinum, to intensify the action of oxygen, or, according to the ozone theory, to ozonise oxygen, without attaching the oxygen to itself. (Kühne and Scholz, Virch. Arch. xxxiii. p. 96.)

Place of Oxidation.

It has not as yet been decided whether the oxidations for which the oxygen of the blood is destined, take place in the blood only, or in the tissues only, or in both. On the one hand, we know that muscular and, probably, all other tissues continue to respire, as it is said (that is, to absorb oxygen and produce carbonic acid), even when totally deprived of blood; and actions probably requiring oxygen, muscular contractions, for example, take place when the blood contains no oxygen at all, as in asphyxia (Setschenow). On the other hand, the experiments of Harley (Proc. Roy. Soc. viii. p. 78; xiii. p. 157) show that blood itself removed from the body will continue to absorb oxygen and exhale carbonic acid, and that this "respiration" is affected by various physical and chemical agents. Sachs, too (Arch. Anat. Phys. 1868 p. 345), finds that, after removal from the body, blood secluded from air gains in carbonic acid (both loose and fixed) and loses oxygen, but his experiments are open to objections. Nawrocki also arrives at the same result (*op. cit.*). Estor and Saintpierre (Robin's Jour. ii. 302) find that the oxygen of arterial blood (determined by the carbonic oxide method) diminishes the farther the artery is situate from the lungs. Thus for 100 vols. they found in the carotid artery 21·06, in the renal 18·22, in the splenic 14·38, in the crural 7·62 vols. of oxygen. They argue that oxidations of respiration take place exclusively in the blood and are most active in the arterial system. Yet the capability of the blood for oxidising oxidisable substances directly injected into it seems very limited.

Qualities of Expired Air.

1. Volume.—The volume of air given out by an expiration is found to be less than that taken in by a corresponding inspiration, when both are dried and measured at the same temperature. This difference, due to the fact that the whole of the oxygen absorbed does not reappear in the carbonic acid exhaled, is variable, but may be said to amount on the average to $\frac{1}{40}$ or $\frac{1}{50}$ of the total volume.

2. Temperature.—The temperature of expired air naturally approaches that of the lungs, the exact degree depending on the relation of the temperature of the atmosphere to that of the blood, on the mode and rate of breathing, the extent and duration of the breath, &c. According to Valentin and Brunner, it is 29·8° for a surrounding temperature of 6·3°, 37·25° for 19·5°, 38·1° for 41·9°. For 22°, Gréhant (Robin's Journal, i. p. 523) puts it at 35·3° when inspiration is made through the nose, 33·9° when through the mouth.

3. Moisture.—The air as it returns from the lungs is laden with watery vapour; saturated, for its own temperature, according to Valentin, not much more than half saturated according to others (Moleschott). Gréhant states that it is saturated for 35°. E. Smith (Phil. Trans. 1852) found it during fasting to be little more than half saturated. The total quantity of water contained in the air expired by the human body during 24 hours has been estimated at 385—773 grms. (Valentin), 557 grms. Gréhant. The total quantity of water passing away within the 24 hours from the human body, as aqueous vapour of expired air, varies greatly, being affected by the temperature of the atmosphere and of the body, by atmospheric humidity and pressure, condition of the organism, &c.

4. Oxygen and carbonic acid.—The decrease of the oxygen and the increase of the carbonic acid is shown by the following average composition of 100 volumes of—

	Oxygen.	Nitrogen.	Carbonic acid.
Atmospheric air	20·81	79·15	·04
Expired air	16·033	79·557	4·380.

In rough numbers, air may be said to lose from 4 to 5 per cent. of its oxygen and to gain from 3 to 4 per cent. of carbonic acid by being breathed. For further details see below.

5. Nitrogen.—W. Edwards found an exhalation of nitrogen in warm weather, an absorption in cold. Regnault and Reiset (Ann. Ch. Phys. 1849, [3], xxvi. 32) concluded from their experiments that warm-blooded animals, living on an ordinary diet, constantly exhaled a small quantity of nitrogen, which was never greater and often much less than $\frac{1}{50}$ of the total weight of oxygen consumed. In frogs, the amount either exhaled or absorbed was too small to be appreciated. In fishes Humboldt and Provencal remarked a constant absorption of nitrogen. An exhalation of nitrogen is constantly observed in animals breathing an atmosphere free from that gas, and W. Müller (*op. cit.*) observed an exhalation of nitrogen when rabbits were made to breathe a limited amount of air. More recently Reiset (Ann. Ch. Phys. [3] lxix. p. 129) found that sheep exhaled from 5—8 grms., calves from 6 – 7 grms., pigs about 1 grm., and turkeys 2 grms. in the 24 hours. In these experiments, as in the earlier ones of Regnault and Reiset, the respiration of the whole animal and not of the lungs only was studied, and it is possible that some of the animals parted, during their stay in the respiratory chamber, with some of the nitrogen contained in their intestines before the beginning of the experiment. The calculations of Boussingault and Barral led them to think that a very large amount of nitrogen passed from the body through the skins and lungs, but such a conclusion is most probably erroneous (see NUTRITION). Pettenkofer indeed argues that Reiset's results are wholly mistakes, and that the amount of nitrogen exhaled or absorbed by the lungs is too small to be appreciated.

6. Ammonia.—The presence of ammonia in the breath has been affirmed by many observers. Thiry (Zeitschr. Rat. Med. xvii. p. 166) has shown that it can be detected in expired air taken directly from the trachea (so as to exclude the fluids of the mouth as a possible source) when the inspired air had been carefully freed from it. Regnault and Reiset failed to assure themselves of its presence in expired air. Grouven (Fütterungs-Versüche, p. 232) has obtained the following quantities (in grms.), the mean being about ·1 grm. in the 24 hours for 100 kilos. of body-weight, when animals were placed in a "respiration chamber:"

	Man.	Boy.	Fat Ox.	Starved Ox.	Ass.	Dog.	Pig.
Per diem	·0488	·0343	·7218	·0958	·2514	·0398	·2026
Per 100 kilos. per diem	·057	·0910	·1146	·0198	·1344	·1326	·1842

Young animals give out proportionally more ammonia than old, small more than large, fat more than lean.

Lossen (Zeitschrf. Biol. i. 207) places the quantity for man in 24 hours at ·0140 grm.

7. Hydrogen and Marsh-gas.—These gases were observed by Regnault and Reiset, by Reiset, and by Pettenkofer, in the air of the respiration chamber. They probably came from the intestines. (See p. 92.)

8. **Other substances.**—Besides the above-described chief ingredients of expired air, it is probable that there are also minute quantities of perhaps many other bodies, and there are many reasons for thinking that these minute quantities are not without importance. (See p. 96, on the effects of impure air). Their exact nature is at present unknown. **Wiederhold** (Henle u. Meissner Bericht. 1858, p. 316) states that he had detected in the condensed vapour of expired air, chloride of sodium, uric acid, and urates of soda and ammonia! The fluid obtained by condensing the vapours of expiration rapidly putrefies.

Cutaneous Respiration.—In man and the higher animals a slight interchange between the gases of the blood and the atmosphere takes place through the skin. There is an exhalation of carbonic acid, and probably an absorption of oxygen. The following table is by **Scharling** (from Gorup-Besanez):—

		Body-weight in kilos.	Carbonic acid in grammes. By lung and skin in 1 hour.	Carbonic acid in grammes. By skin in 1 hour.
Boy	9¾ years	22·0	20·338	0·181
Youth	16 „	57·75	34·280	0·181
Man	28 „	82·	36·623	0·373
Girl	10 „	23	19·162	0·124
Woman	19 „	. . .	. .	0·272

When **Regnault** and **Reiset** examined the products of cutaneous respiration by placing an animal in a bag with the head free, and passing a current of air through the bag, they obtained the following results:—

	Weight.	Duration of exp.	Total quantity of carbonic acid in grms. during time of exp. By skin only.	Total quantity of carbonic acid in grms. during time of exp. By skin and lungs.
Fowl	1940 grms.	8h. 40m.	·336	18·62
„	„	7h. 30m.	·076	16·13
„	„	8h. 45m.	·164	18·70
Rabbit	2425 „	8h. 15m.	·358	20·63
„	„	7h. 45m.	·197	19·38
Dog	4159 „	7h. 50m.	·136	39·15
„	„	8h. 30m.	·176	42·50

When the animal (with head free) was placed in a closed bag for some hours, an examination of the air of the bag at the end of the experiment gave the following results:—

	Length of time.	In 100 vols. of air of bag. CO_2.	In 100 vols. of air of bag. O.	In 100 vols. of air of bag. N.
Fowl as above	8h.	·27	20·76	78·97
Rabbit „	8h.	·36	20·55	79·09
Dog „	8h. 10m.	·29	20·67	79·04

Among the lower animals the skin takes a much larger share in the general respiration. Thus frogs, which uninjured were consuming oxygen at the rate of ·063 (*bis*) ·089, ·103, ·05 grms. per kilo. per hour, continued to consume at the rate ·047, ·063, after their lungs had been cut away; that is to say, they respired nearly as well without their lungs as with them.

Intestinal Respiration.—**Planer** (Wien. Akad. Ber. xlii. p. 307) found the intestinal gases of a dog (killed a few hours after food) to have the following percentage composition:—

		C.	N.	O.	H.	SH^2.
Fed on Meat.	Gas of Stomach	25·20	68·68	6·12		
„	„ Small Intestine	40·1	45·52	trace ?	13·86	
„	„ Large Intestine	74·19	23·0	0·63	1·41	·77
Fed on Pulse	„ Stomach	32·91	66·30	·79		
„	„ Small Intestine	47·34	3·97	. .	48·69	
„	„ Large Intestine	65·13	5·9	. .	28·97	

Ruge (Wien. Akad. Ber. xliv. p. 739) found *flatus* of man, obtained per rectum, to be as follows, in 7 experiments on 3 persons:—

	A.				B.		C.
Carbonic acid	14·94	40·51	21·86	12·77	21·59	54·12	11·87
Nitrogen	45·31	17·50	44·42	43·10	41·82	22·45	40·69
Marsh-gas	39·75	19·77	32·93	44·13	17·52	8·67	47·44
Hydrogen	. .	22·22	0·79	. .	19·07	14·76	

with traces only, and that not always, of sulphuretted hydrogen.

The nitrogen in these cases was probably due to air which had been swallowed, and which had lost its oxygen chiefly within the stomach. The intestines are probably the source of the marsh-gas and hydrogen met with when the respiration of the whole body has been examined. Reiset (*op. cit.*) found in sheep and calves as much as 1 to 2 litres of marsh-gas exhaled per hour, while pigs gave only ·134, ·097 litres of marsh-gas, and ·628 litres hydrogen per hour.

It may seem extravagant to speak thus of an intestinal respiration, yet in some animals this is really an important function. Thus the loach (*Cobitis fossilis*) is in the habit of rising to the surface of water, where it swallows air. In descending it emits from the vent bubbles of gas, which when examined are found to contain only from 12 to 7 per cent. of oxygen, and from 1 to 2 per cent. of carbonic acid. During this process of atmospheric deglutition, the gills are temporarily inactive. It appears that this creature thus obtains a supply of oxygen, which being absorbed from the intestine is consumed by the tissues, the carbonic acid resulting being exhaled chiefly by the gills or skin, and only to a small extent by the vent. (Baumert, An. Ch. Pharm. lxxxiii. p. 1.)

Air-bladder of Fishes.—Many fishes possess an air-bladder (either with or without a pneumatic duct), the contents of which consist of nitrogen, a very small quantity of oxygen in the case of freshwater fishes, a larger quantity in sea-fishes, especially in those dwelling at great depths, and a trace of carbonic acid (Owen). Moreau (Compt. rend. 1863, pp. 37, 816) finds in the air-bladder of the perch 19—25 per cent. of oxygen, of the tench 8 per cent., wholly disappearing when the fish is asphyxiated. The amount of carbonic acid never exceeds 3 per cent. When the air-bladder of a fish possessing a pneumatic duct is exhausted by means of the air-pump, and the animal is replaced in water, the quantity of oxygen in the air-bladder is found in a short time to be very much increased, probably by diffusion from the blood. The percentage may temporarily reach 60 or even 87.

Eggs.—The respiration of hens' eggs has been studied by Baumgärtner (Henle u. Meissner, 1861, p. 304). The following table gives in grms. the changes of 24 hours on several days of incubation of a single egg (initial weight about 55 grms.):—

Day.	Loss of weight.	CO^2 exhaled.	O absorbed.	Water exhaled.
1st	·125	·009	·0074	·123
5th	·232	·016	·0149	·230
10th	·100	·050	·0325	·082
15th	.134	·290	·2355	·079
20th	·212	·56	·4435	·095
21st (hatched)		1·008	·7317	

Variations in the Quantity of Carbonic Acid exhaled.

1. Dependent on the mode of breathing.

In a single breath the air at the beginning of an expiration is poorer in carbonic acid than towards the close; this difference disappears when, after completion of an inspiration, the breath is held for 40 seconds before commencing the expiration.

Inspiration having been made, the longer the breath is held before beginning the expiration, the greater is the percentage of carbonic acid in the expired air. Thus, with an inspiration of 4560 cc. and with pauses between inspiration and expiration of 0, 20, 40, 60, 80, 100 seconds respectively, the percentage of carbonic acid was found by Becher to be 3·6, 5·6, 6·3, 7·2, 7·3, 7·5. The increase of carbonic acid diminishes rapidly with the duration of the pause; and 7·5 or 8 per cent. may be taken as the limit of the amount of carbonic acid present in the deeper layers of the air in the lungs.

During a given time, and for the same rate of breathing, the deeper the breath, the less is the percentage of carbonic acid in the expired air, but the greater the total quantity exhaled.

For a constant depth of breath, the quicker the rate of breathing, the less is the percentage, but the greater the total quantity of carbonic acid exhaled.

2. Dependent on extrinsic conditions.

Temperature.—With cold-blooded animals (frogs), the quantity of carbonic acid exhaled varies directly as the temperature (Moleschott, Untersuch. ii. 315). The same law holds good with mammalia passing in or out of the state of hybernation. With warm-blooded creatures in general, the amount of carbonic acid varies inversely as the temperature, when the latter is neither too low nor too high to injure the economy (Letellier Vierordt). The observations of E. Smith (Phil. Trans. 1859), on the influence of temperature as manifested in the effects of seasons, while leading to the same conclusion, show "that there is no absolute relation between a given temperature and the quantity of carbonic acid exhaled."

Pressure.—The influence of pressure has not been exactly determined. According to **Hervier** and **St. Lager**, the quantity of carbonic acid increases with the atmospheric pressure up to 773 mm., beyond which it decreases. **E. Smith** observed an inverse relation between pressure and carbonic acid, which however was very general only, and subject to marked exceptions.

Light.—Frogs exhale more carbonic acid in a strong than in a weak light. (**Moleschott.**)

Humidity of the atmosphere increases the quantity of carbonic acid. (**Lehmann.**)

Seasons.—**E. Smith** observed that the amount of carbonic acid expired began to decline in early June and continued to do so till September. In October the amount began to rise, and continued to do so with more or less uniformity during the winter months. Spring is the season of the greatest and autumn that of the least activity of the respiratory functions. The influence of seasonal changes is one that cannot be explained solely by reference to changes in temperature and barometric pressure.

Changes in the nature of inspired air.—When the amount of **carbonic acid** in the inspired air is increased beyond that proper to the atmosphere, the quantity of carbonic acid exhaled is proportionately decreased. **W. Müller** found that when rabbits were made to breathe a limited amount (150—250 cc.) of oxygen they consumed the whole of the gas. At first they took in the oxygen and gave out carbonic acid; but through the diminution of the volume of the gas at their disposal, caused by the consumption of oxygen, the tension of the carbonic acid that had been expired became so much increased as after a while to exceed the tension of the carbonic acid in the blood. Hence not only the exhalation of carbonic acid ceased, but that which had been expired was reabsorbed. When the amount of **oxygen** in the inspired air is increased beyond that proper to the atmosphere, no appreciable increase can be observed in the amount of carbonic acid exhaled (**Regnault** and **Reiset**). When **hydrogen** is substituted for **nitrogen** in the inspired air no essential change in respiration takes place.

3. Dependent on **intrinsic conditions.**

Food: **Abstinence, Hunger.**—All observers agree in stating that during starvation the amount of carbonic acid falls. In **Bidder** and **Schmidt's** experiments on a cat, which endured 18 days' deprivation of food, the amount per diem, except during the first and last days, was remarkably constant for each kilo. of body-weight (though for the whole body it gradually lessened from day to day). (See NUTRITION.) **E. Smith** found, during a 24 hours' fast, the carbonic acid diminished about 25 per cent (7 grains per minute instead of 9·77 grains). The minimum was arrived at within 4½ hours after the last meal, and from that point onward there was no marked decrease; thus indicating the existence of a tolerably uniform "normal" or "basal" line, below which the system does not pass in health. **Pettenkofer** and **Voit** found that their dog passed (30 kilos. *circa*), with 1800 grms. meat and 350 grms. fat, 840·4 grms. of carbonic acid, but after 10 days' fasting only 289·4 grms. **Ranke, J.** (*Tetanus*, p. 234), weight 70 kilos. *circa*, determined, by means of Pettenkofer's apparatus, the total quantity of carbonic acid exhaled by himself during 24 hours under the following circumstances, to be:

	grms. carbonic acid.	grms. carbon.
Starving	662·9	180·8
do.	663·5	180·9
Pure meat diet (1832 grms.)	847·5	231·2
A diet of 150 grms. fat 300 „ starch 100 „ sugar	735·2	200·5
Ordinary mixed diet	791·1	215·7
Mixed diet, as much as possible eaten . .	925·6	252·4
A diet in which the nitrogen of ingesta and egesta were in equilibrium	759·5	207

Meals.—An increase in the production of carbonic acid begins directly after a meal and progresses to a maximum, after which the amount gradually declines to the basal minimum. The maximum was observed in from one to two hours after a meal, and was greatest after breakfast and tea (with a midday dinner). On a day of fasting a slight rise was observed about the times when the influence of meals, if taken, would have been felt. (**E. Smith.**)

Kinds of food.—**E. Smith**, taking the minimum quantity exhaled when fasting in the early morning, has investigated the effects of various articles of food. He finds that the exhalation of carbonic acid is increased by the following "excito-respiratory" articles, which are here placed in a series of decreasing intensity of effect:—Tea, sugars (cane-sugar, milk-sugar, grape-sugar), coffee, rum, milk, cocoa, stout, ale, chicory, casein, gluten, gelatin, albumin. Compound aliments containing several of these substances have an action greater than that of any of their constituents. In most of these instances, the increase in the evolution of carbon was greater than could be accounted for by the amount of carbon contained in the article, ex. tea; in others less, ex. sugar. The effect was evident within a few minutes of partaking of the food, and was not investigated for periods of longer than two hours. Other substances do not increase the carbonic acid, are non-excito-respiratory, ex. starch, fat, brandy, whisky, gin, and the volatile elements of wine, spirits, &c. The influence of water does not seem to have been studied. These observations apply to the, so to speak, superficial effects of the various kinds of food; the ulterior effects of diet will be discussed below.

Sleep.—During sleep the amount of carbonic acid is lessened. In man, the quantity expired per minute when asleep is to the quantity when awake as 1 : 1·84 (E. Smith). During the condition known as hybernation, the diminution in the quantity of carbonic acid exhaled is exceedingly marked. Thus a hedgehog, which when awake gave 1·352 grms. of carbonic acid per hour, produced when in complete torpor no more than ·066 per hour, and a marmot 1·076 and ·0144 respectively. (Valentin.)

Exercise.—The quantity is very largely increased, according to all observers. E. Smith, whose average during the day was 9·77 grains per minute, exhaled 5·94 grains per minute, when lying down but not asleep; 18·1 when walking at the rate of 2 miles an hour; 25·83 at 3 miles an hour; and 43·36 and 42·9 on two occasions when working the treadwheel.

Sex.—Men produce a larger quantity of carbonic acid than women.

Age.—The quantity of carbonic acid exhaled by children is absolutely less than that given out by adults, but compared with the body-weight is greater, as is shown in the following table from Lehmann (Lehrb. iii. 320):—

Subject.	Age.	Body-weight.	Carbonic acid per hour.	Carbonic acid per hour per kilo. of body-weight.
Boy . . .	9¾ yrs.	22·00 kil.	20·338 grm.	·9245 grm.
Girl . . .	10 „	23·00 „	19·162 „	·8831 „
Youth . .	16 „	57·75 „	34·280 „	·5887 „
Young woman .	17 „	55·75 „	25·342 „	·4546 „
Soldier . .	28 „	82·00 „	86·632 „	·4466 „
Man . .	35 „	65·5 „	33·530 „	·5119 „

The same applies to animals.

According to Andral and Gavarret, the quantity produced daily by the male sex goes on increasing, with a sudden rise at puberty, up to about 30 years, remains tolerably stationary until between 40 and 50 years, after which it diminishes, especially beyond 60. In the female sex the amount increases up to puberty, then remains stationary, with temporary increase during pregnancy, until the climacteric, after which it rises up to 60 years and then finally falls.

Consumption of Oxygen.

The whole of the oxygen absorbed by the blood from the inspired air does not always reappear in the carbonic acid of the expiration; in general the amount of oxygen consumed during a given interval is greater than the amount of oxygen contained in the carbonic acid expired during the same time. The difference is not a constant one, but varies according to the nature of the food taken, &c.; it is least marked in herbivora living on their ordinary diet, or in animals fed largely on carbohydrates, and most marked in carnivora or in animals fed largely on a meat diet. Regnault and Reiset found in the carbonic acid exhaled by rabbits fed on carrots, &c., 91·7 per cent. of the oxygen consumed; in dogs fed on meat, 74·5 per cent.; in fowls fed on grain, 92·7 per cent.; in dogs fed on bread, 91·3 and 94·3 per cent.; in fowls fed on meat, 76·7 and 63·6 per cent.; in ducks fed on bread and grain 89·2 per cent., on meat 73·8, on fat 62·3. They also found that herbivora when starving gave the proportion of carnivora, that is, they fed on their own flesh. Thus, rabbits starving afforded 69 per cent., ducks starving 69·3 per cent., and fowls 70·7 and 63·9 per cent. The observations of Pettenkofer (Ann. Ch. Pharm. 1863, Suppl. ii.) on the respiration of the dog led to some very remarkable results. After 16 days' meat diet, 63·7 per cent. of the oxygen consumed reappeared in the carbonic acid expired. During a hunger period of 10 days immediately following, the percentage was on an average 63·5. The dog was then fed for 7 days on meat, at the end of which the oxygen in the carbonic acid expired almost exactly equalled the total quantity consumed. After 8 days' rations of 100 grms. fat only, the result was still the same. The animal being then put on a rich meat diet, on the 4th day, the oxygen in the carbonic acid exceeded that consumed by 17 grms.; on the following days, however, the diet and excretion of urea remaining the same, the consumption of oxygen had increased so much, that on the 13th day the oxygen in the carbonic acid had assumed the standard percentage of 65·1. The animal then being fed on 500 grms. of meat and 200 grms., first of starch and then of sugar, the relations of carbonic acid expired and oxygen consumed became so changed that at last the carbonic acid contained 150 (in a second trial 125) parts of oxygen for every 100 parts of oxygen consumed. These remarkable variations serve, on the one hand, to illustrate the character of the changes going on in the body under the influence of different kinds of food; on the other hand, the great excess of carbonic acid, coinciding with the appearance of 7·2 grms. of hydrogen and 6·3 grms. of marsh-gas, indicates that the carbonic acid was not wholly due to combustion of the tissues or plasma, but perhaps arose in part from fermentation of the food within the alimentary canal (see NUTRITION). Hence the consumption of oxygen and not the production of carbonic acid must be taken as a measure of the activity of the vital processes. The following table shows in grammes the amount of oxygen consumed per hour per kilo. of body-weight by members of the various kinds of animals. It will be seen that small creatures consume more than larger ones for the same amount of body-weight:—

The amount in grammes of oxygen consumed per hour per kilo. of body-weight.

Sheep	(Reiset)	·497	Fowls	(Regnault and Reiset)	1·147
Calves	„	·480	Ducks	„	1·850
Pigs	„	·466	Small Birds	„	11·473
Dogs	(Regnault and Reiset)	1·183	Geese	(Reiset)	·677
Rabbits	„	·918	Turkeys	„	·702
„	(Valentin)	1·714			
Marmots: awake	(Regnault and Reiset)	1·198			
„ torpid	„	·040	Frogs	(Regnault and Reiset)	·034
„ awake	(Valentin)	·973	Lizards	„	·1916
„ light sleep	„	·144	Silkworm	„	1·170
„ quite torpid	„	·0238	Earthworm	„	·1613
Hedgehog: awake	„	1·376			
„ torpid	„	·075			

A curious observation was made by **Regnault** and **Reiset** on the consumption o oxygen by the marmot. These animals when wide awake give in their carbonic acid a percentage of oxygen consumed 76·9, when half asleep 54·7, when completely dormant 39·9. This remarkable deficiency explains how it is that these animals may, while in a dormant state, provided that they do not pass urine, actually increase in weight from formation and retention of water.

Breathing Impure Air.—When an animal is suddenly cut off from its usual supply of air, as by closure of the windpipe, by immersion in water, or by being plunged into some irrespirable (but otherwise innocuous) gas, such as nitrogen or hydrogen, the breathing is at first hurried and laboured, but after a while becomes slow and weak; conciousness is lost, convulsions take place, and death by suffocation or asphyxia is the result. In such cases, the air remaining in the lungs contains a trace only of oxygen with a great excess of carbonic acid, the blood both in the arteries and veins is of a dark colour, holding scarcely any oxygen but a very large quantity of carbonic acid. It is not yet clear how far the phenomena belonging to this particular mode of death are due to the absence of oxygen, or to the increase in carbonic acid, or to both of these causes combined. Some observers witnessed no convulsions or dyspnœa, but only a kind of narcotic poisoning, when animals were made to breathe oxygen containing a great excess of carbonic acid; whereas when they were made to breathe air diluted with nitrogen, dyspnœa came on as soon as the proportion of oxygen fell below 5 per cent. These experiments seem to show that the dyspnœa of asphyxia arises from the lack of oxygen. But other observers have found dyspnœa and convulsions to follow the inhalation of oxygen containing 10 per cent. of carbonic acid, and the opinion that carbonic acid is an excitant of muscular and other actions has many supporters.

Similar results are produced more gradually when an animal is confined in a limited space without renewal of air, and has therefore to breathe the same air over and over again. In such cases life is prolonged if the carbonic acid be absorbed by potash as soon as it is formed. If at the death of the animal the air is examined, it is found to contain from 5 to 7 per cent. of oxygen and from 10 to 12 per cent. of carbonic acid (**Bernard**). These figures may be taken to represent the limit, in either direction, at which air ceases to be respirable. When animals or human beings remain for any length of time in ill-ventilated crowded rooms, the resulting impurity of air produces symptoms of discomfort and stiffening, and may, as in some well-known instances, lead to fatal results. These minor ill-effects are in part due to lack of oxygen and increase of carbonic acid, but it is highly probable that they are chiefly owing to the exhalation of various (unknown) substances from the skin and lungs. According to Pettenkofer it is possible to breathe an atmosphere containing 1 per cent. of *pure* carbonic acid for a length of time without any injurious results following, or indeed any discomfort being felt. But 1 per cent. of carbonic acid may be fairly taken as a limit of the impurity of air due to bad ventilation, and respired air containing a much smaller quantity is found to be unbearable. The effects, moreover, which have been described as resulting from the inhalation of small quantities of carbonic acid (Smith) are distinct from those resulting from ordinary impure air. The latter, too, may be imitated by breathing respired air freed from its carbonic acid, and containing therefore the other impurities only; by experimenting on animals, fatal results may be produced. At the same time the carbonic acid may be taken as an indirect measure of the impurity of respired air, and accordingly air which by respiration has acquired more than ·08 per cent. of carbonic acid should be considered as unfit for further respiration. M. F.

RETENE. $C^{18}H^{18}$.—A hydrocarbon polymeric with benzene, discovered in 1837 by Fikentscher and Trommsdorff, and examined chiefly by Fritzsche (J. pr. Chem. lxxv. 281; Jahresb. 1860, p. 475; Gm. xviii. 8). It occurs in thin unctuous scales on fossil pine-stems, in beds of peat and lignite in Denmark and other localities, and together with fichtelite on the Fichtelgebirge, and at Utznach in the Canton of St. Gall. It is produced also by the dry distillation of very resinous pine and fir-wood, passing over together with the heavy tar-oil, and separating in scales like paraffin (Krauss, Ann. Ch. Pharm. cvi. 391). By submitting colophony to dry distillation, and passing the vapour through a red-hot tube, Fritzsche obtained several hydrocarbons, forming compounds with picric acid, amongst them probably retene. *Retisterene*, or *Metanaphthalene* (p. 98), which is obtained in a similar manner by Pelletier and Walter (Ann. Ch. Phys. [2] lxvii. 296), is perhaps impure retene. (Fritzsche.)

Preparation: From fossil wood.—The comminuted wood is exhausted by boiling with alcohol; the greater part of the alcohol is then distilled off; and the remainder of the decoction is evaporated to dryness, and treated with sulphide of carbon, which dissolves retene and other substances, leaving a red-brown acid resin. On removing the sulphide of carbon by distillation, and dissolving the residue, together with picric acid, in benzene, a compound of retene with picric acid and benzene separates out in yellow needles on cooling. These are pressed and recrystallised from alcohol, with addition of excess of picric acid, the compound of retene and picric acid is decomposed by ammonia, and the separated retene is recrystallised from alcohol. (Fritzsche.)

Retene forms soft shining unctuous laminæ, inodorous, tasteless, sinking in cold but floating in boiling water (Fritzsche). It melts at 98—99° (Fehling, Ann. Ch. Pharm. cvi. 388). According to Fritzsche, melted retene solidifies at 90°, the temperature rising to 95°. It evaporates gradually in the air and over the water-bath, and when melted gives off white clouds, which condense to a woolly sublimate (Krauss, Ann. Ch. Pharm. xxviii. 345). It boils at about the boiling-point of mercury, and distils almost unchanged (Fritzsche, Fehling). It is insoluble in *water*, dissolves slowly in cold, much more readily in boiling *alcohol*, easily in warm *ether*, and in *oils*, both *fixed* and *volatile*.

Retene burns with a bright but smoky flame. It is converted into resinous products by treatment with *chromic acid*, with *hydrochloric acid* and *chlorate of potassium*, and with strong *nitric acid*. With more dilute nitric acid, it also forms crystalline products. (Fehling.)

By prolonged contact with strong *sulphuric acid*, retene is converted into retene-disulphuric or disulphoretetic acid, $C^{18}H^{18}S^2O^6$, which crystallises in a solid mass and forms a soluble *barium-salt*, $C^{18}H^{16}Ba''S^2O^6$, crystallising in needles. The *lead-salt*, $C^{18}H^{16}Pb''S^2O^6$, dissolves slightly in cold, easily in boiling water, and separates therefrom in white flocks.

A solution of retene in moderately dilute sulphuric acid deposits on standing, crystals containing $C^{18}H^{18}S^2O^6.5H^2SO^4$.

Retene heated with strong sulphuric acid is converted into the compound $C^{18}H^{20}SO^4$, called by Fritzsche sulphoretene, which separates from boiling water in thin laminæ, from alcohol as a sandy powder or in crusts; is decomposed by heat and forms a crystalline compound with hydrochloric, oxalic, and picric acids.

Retene with Picric acid.—A solution of 1 pt. retene and 3 pts. picric acid, in hot alcohol or ether, deposits on cooling, delicate woolly orange-yellow needles of the compound $C^{18}H^{18}.C^6H^3(NO^2)^3O$, which is partially decomposed by alcohol of 90 per cent., completely by more dilute alcohol, into picric acid and retene.

A mixture of retene and picric acid dissolved in hot *benzene*, deposits on cooling needles of the compound $C^{18}H^{18}.C^{6}H^{6}.C^{6}H^{3}(NO^{2})^{3}O$, which on exposure to the air becomes opaque, and gives off the whole of the benzene. (Fritzsche.)

RETENE-SULPHURIC ACID. See the last article.

RETINALITE. A green translucent variety of serpentine from Canada, having a resinous aspect. (See SERPENTINE.)

RETINAPHTHA. Syn. with toluene or hydride of benzyl (i. 573).

RETINASPHALT. A fossil resin of yellow-brown colour, earthy aspect, rarely dense and shining; of specific gravity 1·07 to 1·35; fusible, burns with a white flame, and aromatic odour. Retinasphalt from the lignite of Bovey in Devonshire, where it was first observed, contains, according to Hatchett (Phil. Trans. 1804, p. 404), 55 per cent. resin soluble in alcohol, 42 per cent. insoluble resin; according to Johnston (Phil. Trans. 1840, p. 347), 13·23 per cent. mineral constituents, 27·45 resin insoluble in alcohol, and 59·23 per cent. soluble in alcohol—the latter constituting Johnston's *retinic acid*. Retinasphalt from Halle contains, according to Bucholz (Schw. J. i. 290), 91 per cent. easily soluble resin, and 9 per cent. insoluble resin, resembling amber; that from Cape Sable, United States, contains 42·5 per cent. easily soluble resin, 55·5 per cent. insoluble resin, and 1·5 ferric oxide and alumina. (Troost.)

RETINIC ACID. The portion of retinasphalt from Bovey, which is soluble in alcohol (Johnston). It remains, on evaporating the alcoholic solution, as a yellow-brown resin, which melts, with loss of weight, at 120°, and gives off gas-bubbles at 205°. It dissolves abundantly in ether, whence it is for the most part precipitated by alcohol, sparingly in alcohol, and is precipitated by water. The alcoholic solution gives a slight precipitate with chloride of calcium, more abundant with alcoholic acetate of lead. The acid contains, at 100°, 75·03 per cent. C, 8·77 H, and 16·20 O: after fusion, 77·08 C, 8·70 H, and 14·22 O; the calcium-salt yielded 10·26 per cent. lime, the silver-salt 41·78 to 43·58 per cent. silver-oxide. From these results Johnston deduced the formula $C^{40}H^{54}O^{6}$.

RETINITE. *Walchovite.* A fossil resin found in the coal-mines of Walchow, in Moravia, in rounded lumps, varying in size from that of a pea to that of a man's head. It is brittle, of specific gravity 1·035 to 1·069, has a yellow colour, a conchoïdal fracture, and fatty lustre. At 140° it becomes translucent and elastic without fusing, and at 250° melts to a yellow oil. By dry distillation it yields combustible gas, tar, and aqueous formic acid. Alcohol extracts from it 1·5 per cent., and ether 7·5 per cent. of resin, both the resins thus obtained being transparent, yellow, and tough. It dissolves slightly in sulphide of carbon, and in boiling rock-oil, but softens in the former. Contains 80·40 per cent. C, 10·68 H, and 8·74 O, agreeing approximately with the formula $C^{40}H^{62}O^{3}$. (Schrötter, Pogg. Ann. lix. 61: see also Cerutti, N. Br. Arch. xxii. 286.)

The lignite of the Wilhelmszech mine, in the Westerwald, contains reddish-yellow brittle deposits of retinite. Branchite or scheererite likewise changes to a resin, which has the colour and soft waxy consistence of retinite. (Casselmann.)

The name retinite is used by Rammelsberg (*Mineralchemie*, p. 966) as a generic name for fossil resins containing oxygen.

RETINOLE and **RETINYL.** Hydrocarbons obtained in the rectification of the products of the dry distillation of turpentine-resins (Pelletier and Walter, Ann. Ch. Phys. [2] lxvii. 269). See TURPENTINE.

RETISTERENE. *Metanaphthalene.* A solid hydrocarbon, probably identical with retene, obtained by the distillation of resins, and passing over with the last portions of the distillate. (Pelletier and Walter, Ann. Ch. Phys. [2] lxxii. 296.)

RETORT. This name was originally applied to the well-known vessel, consisting of a bulb and inclined neck, used for distillation: but it is now, especially in technological language, applied to distillatory vessels of other shapes—for example, to the cylinders of iron or earthenware used for the distillation of coal, &c.

RETZBANYITE. A massive grey mineral from Retzbanya, in Hungary, of specific gravity 6·21. It is mixed with oxidised products, and gives by analysis 7·14 per cent. oxygen, 11·93 sulphur, 38·38 bismuth, 36·01 lead, 4·22 copper, and 1·93 silver. (Hermann, J. pr. Chem. lxxv. 450.)

RETZITE. Syn. with EDELFORSITE (ii. 361).

REUSSIN. A salt occurring as an efflorescence at Saidschitz, in Bohemia, and consisting of a mixture of the sulphates of sodium, calcium, and magnesium, with chloride of magnesium [and water], but varying in composition according to the locality and the season of the year. (Reuss, Crell. Ann. 1791, ii. 18.)

RHAMNETIN. $C^{11}H^{10}O^5$. (Gellatly, N. Edinb. Phil. J. vii. 256.)—A pale-yellow crystalline substance, formed, together with glucose, by boiling xanthorhamnin with dilute sulphuric or hydrochloric acid:

$$C^{23}H^{28}O^{14} + 3H^2O = C^{11}H^{10}O^5 + 2C^6H^{12}O^6.$$

A similar transformation takes place when Persian berries, which contain xanthorhamnin, are stirred up with cold water, the rhamnetin being deposited from the filtrate as a yellow powder.

Rhamnetin is nearly insoluble in water, easily soluble in alkalis, and precipitated therefrom by acids; insoluble in alcohol and ether. Hlasiwetz regards it as identical with quercetin (p. 4).

RHAMNIN. (Fleury, J. Pharm. xxvii. 226.—Winckler, Jahrb. pr. Pharm. xxiv. 1.—Binswanger, Repert. Pharm. civ. 54.—Gm. xvi. 80).—A yellow substance contained, together with rhamnocathartin, in the unripe berries of the buckthorn (*Rhamnus catharticus*). It may be prepared by pressing the berries to remove the juice, boiling the residue repeatedly with water, setting the decoctions aside to crystallise, and purified by recrystallisation from boiling alcohol, with aid of animal charcoal. It forms rounded groups of pale-yellow granules or, more rarely, tufts of needles. It is decomposed by heat, is nearly or quite insoluble in cold water, swells up in boiling water, dissolves sparingly in cold, easily in boiling alcohol, but is insoluble in ether. It dissolves easily in alkalis, and is precipitated therefrom by acids; dissolves with saffron-yellow colour in strong hydrochloric or sulphuric acid, and is precipitated by water; in hot nitric acid, forming a dark-brown solution, which becomes yellow on continued heating, and then leaves on evaporation a crystalline mass, mostly soluble in water, together with a bitter yellow powder, probably picric acid.

The name rhamnin is applied also by Ortlieb (Mulhous. Soc. Bull. xxx. 16) to a product obtained from Persian berries. According to his observations, the aqueous decoction of the berries, after the colouring-matter has separated from it, contains a large quantity of sugar, and after fermentation deposits yellow crystalline grains of *hydrate of oxyrhamnin*, $C^{21}H^{18}O^{11}$, isomeric or perhaps identical with euxanthic acid (ii. 609), then yellow-green flocks of *hydrate of rhamnin*, $C^{21}H^{18}O^{10}$; and the mother-liquor, if boiled with sulphuric acid, yields flocks of *rhamnin*, $C^{21}H^{16}O^9$. These results, however, do not agree with those obtained by Kane and by Gellatly (p. 100). See also XANTHORHAMNIN.

RHAMNOCATHARTIN. *Cathartin.* (Hubert, J. Chim. méd. vi. 193.—Winckler, Jahrb. pr. Pharm. xix. 221; xxiv. 1.—Binswanger, Repert. Pharm. civ. 54.—Gm. xvi. 81.)—The uncrystallisable bitter principle of buckthorn berries. To prepare it, the juice of the ripe berries is evaporated to an extract; this extract is exhausted with hot alcohol, the tincture evaporated, and the residue mixed with water, which separates yellow-green pulverulent rhamnotannic acid. The filtrate, shaken up with coarsely-pounded, purified bone-charcoal, as long as it retains any bitter taste, yields rhamnocathartin to the charcoal; and on washing this charcoal with cold water, drying, treating it with hot alcohol, and evaporating the tincture, the rhamnocathartin is left behind. (Binswanger.)

Rhamnocathartin is a translucent, amorphous, yellowish, brittle mass, which emits a peculiar smell when rubbed. It has a bitter and very repulsive taste, is neutral, and tolerably permanent in the air. When heated, it melts to a yellow oil, turns brown, gives off inflammable vapours, and leaves combustible charcoal. With *nitric acid*, it yields a large quantity of picric acid (Winckler). It is not decomposed during the fermentation of the juice. (Hubert.)

It is soluble in all proportions in *water* (Winckler), insoluble in cold, somewhat soluble in boiling water, to which it imparts a very bitter taste, while the remainder melts and adheres to the sides of the vessel. The hot solution becomes turbid on cooling (Binswanger). The aqueous solution is coloured brownish gold-yellow, without precipitation, by *ammonia*, the *fixed alkalis*, and *basic acetate of lead*, and becomes colourless again on addition of acids. It colours *ferric chloride* dark-brown-green. (Winckler.)

Rhamnocathartin dissolves in all proportions in *alcohol*, but is insoluble in *ether*.

RHAMNOTANNIC ACID. (Binswanger, *loc. cit.*)—Obtained, as above, in the preparation of rhamnocathartin, and purified by washing, drying, solution in ether, and evaporation.—It is a neutral, greenish-yellow, amorphous, easily friable mass; tastes bitter and astringent; melts and decomposes when heated; is nearly insoluble in cold water, somewhat soluble in boiling water, and in aqueous ammonia, forming a golden-yellow liquid which gradually turns brown. With lime-water and potash-ley it forms yellow solutions, which do not change in contact with the air; the former, however, gradually deposits yellow flocks. The aqueous solution, added to neutral or basic acetate of lead, throws down orange-yellow flocks; it colours ferric salts olive-green, and then precipitates them. In tartar-emetic it forms, after some time, a yellow precipitate; does not precipitate solution of gelatin. The acid dissolves readily in alcohol and ether.

RHAMNOXANTHIN. A yellow, crystalline, sublimable substance identical with *Frangulin*, under which name it has already been described (ii. 706). It exists in the root, bark, and stem-bark of *Rhamnus Frangula* (Buchner, Binswanger), and according to Phipson (Compt. rend. xlvii. 153), in the bast, and in the vessels of the medullary sheath of the branches. Phipson prepares it by macerating the branches for three or four days in sulphide of carbon, evaporating the extract to dryness, exhausting the residue with alcohol, which leaves fat undissolved, again evaporating, and recrystallising from ether.

RHAMNUS. The several species of *Rhamnus* yield yellow or green colouring-matters, which have been examined by different chemists, not always with accordant results:—

1. Persian or Turkey-berries, the seeds of *Rhamnus amygdalinus*, *R. oleoïdes*, *R. saxatilis*, and Avignon-grains, the seeds of *R. infectorius*, which are employed in dyeing for the production of yellow colours, yield: *α*. According to Kane (Phil. Mag. [3] xxiii. 3), in the unripe state, chrysorhamnin, $C^{23}H^{22}O^{11}$ (i. 960), and when ripe, xanthorhamnin, $C^{23}H^{24}O^{14}$.—*β*. According to Gellatly, xanthorhamnin, $C^{23}H^{28}O^{14}$, with rhamnetin, $C^{11}H^{10}O^{5}$, as a product of its decomposition.—*γ*. According to Ortlieb (Mulhous. Soc. Bull. xxx. 16), rhamnin, $C^{21}H^{16}O^{9}$, hydrate of rhamnin, $C^{21}H^{18}O^{10}$, and hydrate of oxyrhamnin, $C^{21}H^{18}O^{11}$.

2. The bark of the berry-bearing alder (*Rhamnus Frangula*), and of the buckthorn (*R. catharticus*), yields the yellow dye called rhamnoxanthin by Buchner and Binswanger, frangulin by Casselmann.

3. The berries of *R. catharticus* yield the rhamnin of Henry, Winckler, and Binswanger (p. 99); also Binswanger's rhamnocathartin, called cathartin by Hubert (p. 99). These berries and the syrup prepared from them possess purgative properties; but their action is violent and dangerous, so that their use in medicine is not to be recommended.

The berries of some species of rhamnus are used for dyeing morocco-leather of a yellow colour; others for dyeing wool; and the bark of some is employed for striking a black with salts of iron. Those of *Rhamnus catharticus* yield the pigment called sap-green, or bladder-green; and recently M. Charvin of Lyons has obtained from them a splendid green dye called *Vert Venus*, *Vert-Azof*, or *Vert-Lumiere*, identical with, or very similar to, the Chinese Lo-Kao. (See DYEING, ii. 358; also Wagner's Jahresbericht, 1861, p. 567.)

RHAPONTICIN. Syn. with CHRYSOPHANIC ACID (i. 958).

RHEADIC ACID. According to Leo Meier (Repert. Pharm. [3], xli. 325), the red colouring-matter of the flowers of the common red poppy (*Papaver Rheas*) consists of two acids, called *rheadic* and *papaveric acid*, separable by neutral acetate of lead, which precipitates only the former; they do not appear to have been obtained pure. (See *Gmelin's Handbook*, xvi. 527.)

RHEIC ACID.
RHEIN. } Syn. with CHRYSOPHANIC ACID (i. 958).

RHEOMETER. Syn. with GALVANOMETER. (See ELECTRICITY, ii. 443.)

RHEOSTAT. An instrument for regulating and measuring the force of electric currents. (See ELECTRICITY, ii. 464.)

RHEUM. See RHUBARB (p. 107).

RHEUMIN. Syn. with CHRYSOPHANIC ACID (i. 958).

RHODANIDES. A name applied to sulphocyanates, on account of the red colour which they produce with ferric salts.

RHODEORETIN. Syn. with CONVOLVULIN (ii. 15).

RHODEORETINOL.
RHODEORETINOLIC ACID. } Syn. with CONVOLVULINOLIC ACID (ii. 15).

RHODIUM. *Atomic Weight*, 104; *Symbol*, Rh.—A metal belonging to the platinum group, discovered by Wollaston in 1804. He found the ore from Brazil to contain 0·4 per cent., and native platinum from another locality has been found to contain as much as 3 per cent. of rhodium. It often occurs in considerable quantity in platinum residues.

Preparation.—1. Platinum-ore is dissolved in nitromuriatic acid; the platinum and iridium are precipitated by sal-ammoniac, and the palladium by cyanide of mercury; the liquid is then saturated with carbonate of sodium; hydrochloric acid is added, to decompose the excess of mercuric cyanide; the liquid is evaporated to dryness; and the residue is treated with alcohol. The whole then dissolves, excepting the chlororhodiate of sodium, which remains as a red-brown powder. This salt, reduced by hydrogen and washed with a large quantity of water, yields pure rhodium.

2. Granular platinum-residue, consisting chiefly of rhodium and iridium, with small quantities of osmium and ruthenium, is treated, as described under IRIDIUM (iii. 315, No. 4), to separate the other metals; and the residue insoluble in nitromuriatic acid, consisting of rhodium with a small quantity of iridium, is mixed with a large excess of common salt, and heated to low redness in a current of dry chlorine, whereby the rhodium is converted into chlororhodiate of sodium, which may be dissolved out by water and crystallised by evaporation. The metal may then be obtained from it by reduction with hydrogen, or by precipitation with zinc: or, better, the concentrated solution may first be mixed with sal-ammoniac, which will throw down any iridium still remaining, and the filtrate evaporated. It then yields fine prisms of chlororhodiate of ammonium, which when calcined leaves pure rhodium. (Frémy.)

3. Platinum-residue, precipitated by metallic iron from the mother-liquors from which platinum has been extracted (iv. 683), is fused at a bright red-heat with 1 pt. lead and 2 pts. litharge; and the regulus thus obtained, after being carefully freed from slag, is treated with nitric acid diluted with an equal volume of water. The pulverulent mass which remains undissolved is then heated to redness with 5 pts. of barium-peroxide; the ignited mass is treated with water, and then with nitromuriatic acid (which eliminates osmic acid); the barium is precipitated from the solution by sulphuric acid, the quantity required having been previously calcinated; the liquid is heated to the boiling-point, and filtered; the filtrate is evaporated to dryness at 100°, with addition, first of a little nitric acid, then of a large quantity of sal-ammoniac; and the solution is washed with a strong solution of sal-ammoniac, which dissolves out all the rhodium. The filtered liquid is then heated with a large excess of nitric acid (to decompose the sal-ammoniac), and finally evaporated to dryness in a porcelain crucible; and the rhodium-salt thus obtained, after being moistened with sulphide of ammonium, is mixed with three or four times its weight of sulphur, and heated to bright redness in the covered porcelain crucible, enclosed for the purpose in an earthen crucible, the space between the two being filled up with powdered charcoal. There then remains a regulus of metallic rhodium, which may be purified by continued boiling with nitromuriatic acid, and then with strong sulphuric acid. To obtain the metal quite pure, it is fused at a low red-heat with 3 or 4 pts. of metallic zinc, and the fused and cooled mass is treated with concentrated hydrochloric acid, which leaves undissolved a crystalline alloy of the two metals. This alloy is dissolved in nitromuriatic acid; the solution is mixed with ammonia, till the precipitate formed at first is redissolved, then boiled and evaporated, whereby a yellow precipitate is formed, consisting of ammoniochloride of rhodium, $5NH^3.RhCl^3$; and this salt, after being purified by recrystallisation, is calcined with a small quantity of sulphur, in a graphite crucible, at a very strong red-heat. Metallic rhodium then remains, which may be fused in the oxyhydrogen furnace (iv. 313). (Deville and Debray, Ann. Ch. Phys. [3], lvi. 385; Jahresb. 1850, p. 238.)

According to Claus (J. pr. Chem. lxxxv. 129; Jahresb. 1861, p. 327), the above-described method of disintegration with peroxide of barium does not give good results; because the rhodium, though oxidised thereby, is rendered very difficult of solution in acids, and indeed will not dissolve at all, unless iridium is also present, to assist the solution by contact-action. Claus therefore gives the preference to Wöhler's method of decomposition, by mixing the substance with chloride of sodium and igniting it in chlorine-gas (iii. 314). For the separation of the iridium and rhodium in the solution obtained by treating the resulting mass with water, he recommends that the trichloride of iridium be first converted into tetrachloride by boiling with nitriomuriatic acid, and the iridium then separated by fractional precipitation with sal-ammoniac. The mode of separation by digesting the dried saline residue in sal-ammoniac solution, he regards as objectionable; because the rhodium-salt, when once crystallised, dissolves but slowly in that liquid, and adheres obstinately to the iridium-salt, so that a very large quantity of the sal-ammoniac solution is required to dissolve it.

Properties.—Rhodium is a whitish-grey metal, very hard, much less ductile than platinum. It is somewhat more fusible than iridium, but scarcely softens in the flame of the oxyhydrogen blowpipe; it may, however, be fused in Deville's oxyhydrogen furnace (iv. 313). The melted metal absorbs oxygen, and spits as the globule sets. The specific gravity of unfused rhodium is 10·64; that of the pure metal after fusion is 12·1.

Rhodium is unalterable in the air at ordinary temperatures, but oxidises at a red heat, and with great facility if in the state of powder. It combines also with chlorine at a red heat. When pure it resists the action of the strongest acids, even of nitromuriatic acid, but when alloyed with certain metals (as with lead, bismuth, copper, and platinum), it dissolves in nitromuriatic acid, together with those metals; when fused with gold or silver, however, it does not dissolve. It is readily oxidised by fusion with nitre, or with peroxide of barium. By fusion with sulphate of potassium, it is converted into soluble rhodiopotassic sulphate. Mixed with chloride of sodium, and ignited in a stream of chlorine gas, it is converted into chlororhodiate of sodium, which is likewise easily soluble.

RHODIUM, ALLOYS OF. Rhodium unites with most other metals. Some of the alloys, as already observed, dissolve completely in nitromuriatic acid, whereas others yield to this solvent only the metal alloyed with the rhodium. An alloy of rhodium and *gold* found in Mexico contains from 34 to 43 per cent. rhodium. (Del Rio, Ann. Ch. Phys. [2], xxix. 137.)

One pt. of rhodium and 1 pt. of *steel* form an alloy, which has a specific gravity of 9·176, a very fine colour and surface for metallic mirrors, and does not tarnish in the air.—One pt. rhodium with 50 to 100 steel forms a very hard and rather tough alloy, which requires for tempering a heat higher by 39° than common steel, and 17° higher than Indian steel. (Faraday and Stodart.)

Rhodium also unites with *zinc* and *tin*, forming the crystallised alloys, $RhZn^2$ and $RhSn$. (Deville and Debray.)

RHODIUM, CHLORIDES OF. A *dichloride*, $RhCl^2$, is said by Fellenberg to be obtained by heating the corresponding sulphide, RhS, in chlorine-gas; but according to Claus, there is but one definite compound of rhodium and chlorine—viz., the trichloride or rhodic chloride, $RhCl^3$. It is obtained in the anhydrous state by igniting the pulverised metal in a stream of chlorine, or, more easily, by heating one of its double salts (*infra*) for some time with strong sulphuric acid, and pouring the mixture when cold into water, which dissolves the alkaline sulphate and a small quantity of undecomposed double chloride, leaving the rhodic chloride undissolved. As obtained by either process, it is a brownish-red indifferent body, insoluble in all acids and alkalis. When heated with *nitrite of potassium*, it turns yellow, and is resolved into an orange-yellow powder, slightly soluble in water, but easily soluble in hydrochloric acid, and a soluble compound precipitable by alcohol. With *nitrite of sodium* it yields only the soluble salt. *Sulphide of ammonium* added to these solutions, throws down sulphide of rhodium, soluble in excess of the alkaline sulphide, and completely precipitable therefrom by acids. (W. Gibbs, Sill. Am. J. [2] xxxiv. 341; Jahresb. 1863, p. 293.)

Hydrated rhodic chloride, $RhCl^3.4H^2O$, remains in the form of a red-brown vitreous mass, on evaporating over the water-bath a solution of rhodic oxide in hydrochloric acid, previously freed from potash by treatment with nitric acid. It yields a red powder, is deliquescent, soluble in alcohol, insoluble in ether; at a red heat it gives off its water, and becomes insoluble.

Chlororhodiates of Ammonium.—The salt $2(3NH^4Cl.RhCl^3).3H^2O$ is obtained by decomposing the corresponding sodium-salt with sal-ammoniac; it crystallises in fine rhombohedral prisms, easily soluble in water, insoluble in alcohol. The boiling aqueous solution deposits on cooling, prisms and hexagonal plates of the salt $2NH^4Cl.RhCl^3.H^2O$, less soluble and darker-coloured than the preceding.

Chlororhodiates of Potassium.—The salt $3KCl.RhCl^3.3H^2O$, formed by mixing the solutions of rhodic oxide in hydrochloric acid with a strong solution of potassic chloride, crystallises in sparingly soluble prisms, which effloresce and give off all their water on exposure to the air. Another double salt, $2KCl.RhCl^3.H^2O$, is obtained by heating, in a current of chlorine, a mixture of pulverised rhodium or rhodic chloride with chloride of potassium. The black saline mass dissolves in water, and the solution yields by evaporation dark-red crystals soluble in alcohol.

Chlororhodiate of Sodium, $3NaCl.RhCl^3.12H^2O$, is obtained by heating a mixture of 1 pt. rhodium and 2 pts. common salt in a stream of chlorine; it crystallises like the corresponding potassium-salt.

RHODIUM, CYANIDE OF. $RhCy^3$. See CYANIDES (ii. 271).

RHODIUM, DETECTION AND ESTIMATION OF. Rhodium forms only one class of salts, viz. the rhodic salts, corresponding in composition with the trichloride. These salts are for the most part rose-coloured (hence the name of the metal), and exhibit the following reactions in solution:—With *sulphydric acid*, a brown precipitate of sulphide, which is slowly deposited; with *sulphydrate of ammonium*, a brown precipitate, insoluble in excess: with *sulphurous acid* and *sulphites*, a pale-yellow precipitate, affording a very characteristic reaction; with *potash*, a yellow precipitate of hydrated rhodic oxide, soluble in excess; with *ammonia* also a yellow precipitate, which, however, does not form immediately; with *alkaline carbonates*, a yellow precipitate after a while. *Iodide of potassium* produces a slight yellow precipitate; *stannous chloride* imparts a dark colour to the solutions, but forms no precipitate. *Mercurous nitrate* and *nitrate of silver* form with rhodic chloride, precipitates analogous in composition to the argento-iridic chloride already mentioned (iii. 318). *Zinc* precipitates metallic rhodium. In a solution of rhodium mixed with excess of potash, *alcohol* forms, even at ordinary temperatures, a black precipitate, probably consisting of metallic rhodium; with the other platinum-metals, this reaction takes place only when the liquid is heated. No precipitate is formed by sal-ammoniac, chloride of potassium, chromate of potassium, oxalic acid, cyanide of potassium, cyanide of mercury, ferrocyanide or ferricyanide of potassium, or gallic acid. *Hydrogen gas* reduces the anhydrous salts at a moderate heat.

Chlororhodiate of sodium (p 102) forms with soluble *borates*, a yellow precipitate of rhodic oxide, RhO^3, containing the whole of the metal. A similar reaction is produced by *trisodic phosphate* and by *alkaline carbonates*, but part of the rhodium then remains in the solution, giving it a yellow colour. (Claus, Jahresb. 1863, p. 697.)

Estimation and Separation.

Rhodium is estimated in the metallic state. The solution containing it is mixed with excess of sodic carbonate and evaporated to dryness, the residue ignited, and the calcined mass treated with cold water; oxide of rhodium then remains, and may be reduced by hydrogen.

Rhodium is separated from many metals with which it may be alloyed, by fusing the alloy with acid sulphate of potassium; the rhodium is thereby converted into sulphate of rhodium and potassium, which may be dissolved out by water.

The separation of rhodium from other metals in solution is somewhat difficult, because it is not completely precipitated by sulphydric acid. To separate rhodium from *copper*, the solution is saturated with sulphydric acid and left to stand in a stoppered bottle for twelve hours, then filtered, and the filtrate heated to separate an additional portion of sulphide of rhodium. The whole of the precipitate is then roasted in a platinum crucible till the sulphides are completely oxidised, and the product treated with strong hydrochloric acid, which dissolves the copper and leaves the oxide of rhodium. The liquid filtered from the sulphydric acid precipitate still contains a small portion of rhodium, which may be precipitated by carbonate of sodium, and converted into oxide as above. The whole of the oxide is then reduced by hydrogen.

To separate rhodium from *iron*, the rhodium is precipitated as completely as possible by sulphydric acid; the liquid filtered; and the iron in the filtrate precipitated by ammonia, after having been brought to the state of ferric oxide. The iron-precipitate carries down with it a certain portion of rhodium, which may be separated by igniting the precipitate in a current of hydrogen, and treating the reduced metals with hydrochloric acid, which dissolves the iron and leaves the rhodium: the latter is then converted into oxide by ignition in the air. The precipitated sulphide of rhodium is likewise oxidised by roasting. The small quantity of rhodium which remains in solution after precipitation by ammonia is precipitated by carbonate of sodium, and converted into oxide by ignition. The whole of the oxide of rhodium is then reduced to the metallic state by hydrogen.

The separation of rhodium from the alkali-metals is easily effected by converting the metals into chlorides, and igniting the chlorides in a current of hydrogen, which reduces only the chloride of rhodium.

The methods of separating rhodium from the other metals of the platinum-group have already been given (iv. 680—684). The insolubility of chlororhodiate of sodium in alcohol affords in many cases a good mode of separation (p. 101). To separate it from *iridium*, Gibbs (Jahresb. 1863, p. 293) heats the solution of the two metals with excess of nitrite and carbonate of sodium, till a light orange-yellow colour is produced; adds sulphide of sodium by small quantities, till the precipitate of rhodium sulphide begins to redissolve (p. 105); then boils for a few minutes, and mixes the solution when cold with a slight excess of hydrochloric acid. The sulphide of rhodium thereby precipitated is washed with cold water, dissolved in nitromuriatic acid, and the rhodium is converted, first into the double chloride $3NH^4Cl.RhCl^3$, then into the compound $5NH^3.RhCl^3$. (See further Gibbs, Jahresb. 1864, p. 287; and Carey Lea, *ibid.* 291.)

Atomic weight of Rhodium.—3·146 grammes of chlororhodiate of potassium, $2KCl.RhCl^3$, heated in a current of hydrogen, were found by Berzelius (Pogg. Ann. xiii. 435) to lose 0·930 grm. chlorine, leaving a mixture of 0·912 grm. of rhodium and 0·515 of potassium-chloride. In another experiment, 1·3 grm. of the salt lost 0·335 grm. chlorine, leaving 0·358 grm. rhodium and 0·515 grm. potassium-chloride. The mean of these results gives for the atomic weight of rhodium, very nearly the number 104.

RHODIUM, OXIDES OF. Rhodium forms four oxides, having the formulæ RhO, Rh^2O^3, RhO^2, and RhO^3. (Claus.)

The *protoxide*, RhO, is formed, with incandescence, when the hydrated sesquioxide, $Rh^2O^3.3H^2O$, is heated in a platinum crucible. It is a dark-grey substance, perfectly indifferent to acids.

The *Sesquioxide* or *Rhodic Oxide*, Rh^2O^3, obtained by heating the nitrate, is a grey porous mass, with metallic iridescence; insoluble in acids, easily reduced by hydrogen. It forms two hydrates.

The *trihydrate* or *normal rhodic hydrate*, $Rh^2O^3.3H^2O$ or RhH^3O^3, is produced by precipitating a solution of chlororhodiate of sodium with potash, in presence of alcohol; or, without the aid of alcohol, by heating the rhodium-solution with very strong potash-ley. It is gelatinous, shrinks to a very small bulk when dried, and is almost indifferent to acids. Hydrochloric acid, however, dissolves a very small quantity of it, acquiring the fine rose-colour characteristic of rhodic salts.

The *pentahydrate*, $Rh^2O^3.5H^2O$ or $RhH^3O^3.H^2O$, is formed by treating a solution of chlororhodiate of sodium with aqueous potash. It has a lemon-yellow colour, and retains 3 or 4 per cent. potash even after washing. The mother-liquor has a yellow colour, and still retains rhodium.

Dioxide, RhO^2.—Obtained by fusing pulverised rhodium or the sesquioxide, with nitre and potash, and digesting the fused mass with nitric acid, to dissolve off the potash. It is a dark-brown substance, insoluble in acids.

When chlorine is passed into a solution of rhodic pentahydrate, $Rh^2O^3.5H^2O$, a black-brown gelatinous precipitate of the trihydrate, $Rh^2O^3.3H^2O$, is formed at first; but this compound gradually loses its gelatinous consistence, becomes lighter in colour, and is finally converted into a green hydrate of the dioxide, $RhO^2.2H^2O$. The alkaline solution at the same time acquires a deep violet-blue colour.—The green hydrate treated with hydrochloric acid dissolves, with evolution of chlorine, forming a rose-coloured solution of the sesquichloride:

$$2RhO^2 + 8HCl = Rh^2Cl^6 + 4H^2O + Cl^2.$$

Trioxide, RhO^3.—The blue alkaline solution above mentioned deposits, after a while, a blue powder, becoming green when dry, and yielding, when treated with nitric acid, a blue flocculent substance, consisting of the trioxide, easily reduced to the green dioxide. (Claus.)

RHODIUM, OXYGEN-SALTS OF. These salts, analogous in composition to the trichloride, do not crystallise very readily. Moreover, the only rhodic oxygen-salts that can be obtained pure, are those which contain acids capable of expelling nitric acid from its combinations; because, in order to obtain rhodic oxide free from potash, it must be washed with water containing nitric acid, which then unites with the rhodic oxide. The weaker acids are not capable of removing the whole of the potash.

Rhodic acetate, $Rh^2O^3.3C^4H^6O^3.5H^2O = \left.\begin{matrix}(C^2H^3O)^3\\ Rh'''\end{matrix}\right\}O^3.\tfrac{5}{2}H^2O$.—Recently prepared rhodic oxide dissolves in acetic acid, forming an orange-yellow solution, which when evaporated over the water-bath, leaves a transparent orange-yellow, amorphous, non-deliquescent mass, soluble in water and in alcohol; it always, however, retains 3 or 4 per cent. of potash. (Claus.)

Nitrate, $Rh^2O^3.3N^2O^5.4H^2O$ or $\left.\begin{matrix}(NO^2)^3\\ Rh'''\end{matrix}\right\}O^3.2H^2O$.—The yellow hydrate of rhodic oxide dissolves very easily in nitric acid, and the solution evaporated over the water-bath leaves a gummy, very hygroscopic mass, insoluble in alcohol. The nitrate when ignited leaves the insoluble sesquioxide.

Phosphates.—Rhodic oxide dissolves partially in aqueous phosphoric acid, forming the salt $Rh^2O^3.2P^2O^5.6H^2O$, very soluble in water, and precipitable by alcohol. The residue constitutes a basic phosphate.

Sulphate, $Rh^2O^3.3SO^3.12H^2O$, or $\left.\begin{matrix}(S\overset{\prime\prime}{O}{}^2)^3\\ (Rh''')^2\end{matrix}\right\}O^6.12H^2O$.—Yellowish-white crystalline mass, having a styptic and acid taste.—When the mother-liquor of potassio-rhodic cyanide is boiled for some time with strong sulphuric acid, the liquid then evaporated, and the residue digested with water, a potassio-rhodic sulphate dissolves, and another double sulphate remains as a reddish-yellow crystalline powder, consisting of $\left.\begin{matrix}(SO^2)^3\\ Rh'''K^3\end{matrix}\right\}O^6$ (Claus). The same salt is formed when sulphuric acid is added to a solution of chlororhodiate of potassium. (Berzelius.)

Sulphite, $Rh^2O^3.3SO^2.6H^2O$, or $\left.\begin{matrix}(S\overset{\prime\prime}{O})^3\\ (Rh''')^2\end{matrix}\right\}O^6$.—Resembles the sulphate, but is white, soluble in water, insoluble in alcohol. When heated it gives off sulphurous and sulphuric acids, and leaves an oxide of rhodium. A compound of this salt with sulphite of potassium, $3K^2SO^4.Rh^2(SO^3)^3.6H^2O$, may be obtained by treating a solution of chlororhodiate of potassium with excess of acid sulphite of potassium, first at ordinary temperatures, then for a long time at a higher temperature.

RHODIUM, SULPHIDES OF. A *protosulphide*, RhS, is obtained by heating rhodium (Berzelius), or chlororhodiate of ammonium (Vauquelin), with sulphur; also by heating the sesquisulphide in an atmosphere of carbonic anhydride (Fellenberg). It has a greyish-blue colour and metallic lustre (Vauquelin), and melts only at a very high temperature (Berzelius). When heated in a current of dry chlorine, it is converted into the dichloride. (Fellenberg, Pogg. Ann. i. 63.)

Sesquisulphide of Rhodium, Rh^2S^3, is obtained as a black-brown precipitate by the action of sulphydric acid on a solution of an alkaline chlororhodiate.

RHODIUM-COMPOUNDS, AMMONIACAL. These compounds, discovered by Claus (*Beiträge zur Geschichte der Platinmetalle*, Dorpat, 1854; Jahresb. 1854, p. 369; 1855, p. 433), are analogous to the ammoniacal iridium-compounds (iii. 324). A dilute solution of the ammonium-salt, $3NH^4Cl.RhCl^3.\frac{3}{2}H^2O$, mixed with excess of ammonia, assumes a lemon-yellow colour, and deposits a precipitate of rhodic hydrate; and the filtered liquid leaves on evaporation a light-yellow saline residue, from which water extracts sal-ammoniac, leaving a yellow crystalline powder, consisting of the ammonio-trichloride of rhodium, $5NH^3.RhCl^3$, which may be formulated as *chloride of diammo-rhodio-triammonium*, $N^3[(NH^4)^2Rh'''H^7].Cl^3$. It may be purified by dissolving it in boiling aqueous ammonia, and evaporating the filtered solution over the water-bath; and is deposited at a certain degree of concentration, in small transparent prisms, triclinic according to Claus, rhombic according to Keferstein (Jahresb. 1856, p. 421). It is sparingly soluble in water, insoluble in alcohol, soluble without decomposition in potash and in ammonia, slowly and imperfectly decomposed by acids. When heated, it gives off ammonia, sal-ammoniac, and free nitrogen, and leaves metallic rhodium.

The corresponding *oxide*, $10NH^3.R^2O^3$, is obtained by digesting the ammonio-chloride with water and silver-oxide, and evaporating the resulting yellow solution in a vacuum; it then remains in the solid state. It dissolves in acids, forming the corresponding ammoniated rhodium-salts, and expels ammonia from sal-ammoniac.—The *carbonate*, $10NH^3.Rh^2O^3.3H^2CO^3$, is a white, strongly alkaline, saline mass, easily soluble in water, insoluble in alcohol.—The *nitrate*, $10NH^3.Rh^2O^3.3N^2O^5$, is a neutral yellowish-white salt, which does not decompose till heated above 160°.—The *sulphate*, $10NH^3.Rh^2O^3.3H^2SO^4$, forms yellowish-white prismatic crystals, which do not decompose till heated above 180°.—The *oxalate* is also crystalline; the *phosphate* was obtained only as a yellowish gummy mass.

RHODIUM-GOLD. See RHODIUM, ALLOYS OF (p. 102).

RHODIZITE. A mineral supposed to be a lime-boracite, occurring in minute, monometric, tetrahedral crystals, on red tourmalines from the neighbourhood of Mursinsk in Siberia. Hardness = 8. Specific gravity = 3·3 – 3·42. Tinges the blowpipe flame green above and red below, and finally red throughout: hence its name. (G. Rose, Pogg. Ann. xxxiii. 253.)

RHODIZONIC ACID. This name is applied to two acids produced, under different circumstances, from carboxide of potassium (iv. 696). Berzelius and Wöhler noticed that a red substance is produced by the action of water on the black mass formed in the preparation of potassium by Brunner's process (iv. 693). L. Gmelin found that the aqueous solution of this substance yields croconate of potassium when evaporated in contact with the air, and inferred that it contains an acid different from croconic acid. Heller, in 1837 (Ann. Ch. Pharm. xxiv. 1), examined this acid more particularly, and gave it the name of rhodizonic acid. It was further examined by Werner (J. pr. Chem. xiii. 404), but the experiments of these chemists did not determine the composition of the acid. Brodie, in 1859 (Chem. Soc. Qu. J. xii. 269), by treating pure carboxide of potassium with anhydrous alcohol, obtained a red salt, $C^{10}K^6O^8$, which he regarded as rhodizonate of potassium, identical with that previously obtained by Heller and Werner. On the other hand Will, in 1861 (Ann. Ch. Pharm. cxviii. 187), by the analysis of several salts of the acid obtained in a similar manner from the impure carboxide of potassium formed in the preparation of the metal, concluded that its composition is $C^5H^4O^6$, or $C^{10}H^8O^{12}$; and this result is confirmed by the experiments of Lerch (Ann. Ch. Pharm. cxxiv. 20), who has obtained rhodizonic acid in the free state by decomposing the salts of carboxylic acid, $C^{10}H^4O^{10}$ (iii. 190, iv. 296), with acids. It appears then that the name rhodizonic acid has been applied to two distinct compounds. It will be convenient to designate the acid originally obtained by Heller, and analysed by Will and Lerch, as α-rhodizonic, and that obtained by Brodie as β-rhodizonic acid.

α-Rhodizonic acid, $C^5H^4O^6 = \left.\begin{matrix}(C^5HO^3)''' \\ H^3\end{matrix}\right\}O^3$.—This acid is formed from carboxylic acid by the assumption of water: $C^{10}H^4O^{10} + 2H^2O = 2C^5H^4O^6$ (Lerch). When dried in a vacuum it contains $C^5H^6O^7 = C^5H^4O^6.H^2O$, and gives off 1 at. H^2O at 100°. The vacuum-dried acid forms colourless rhombic prisms, easily soluble in water and in alcohol; the colourless acid aqueous solution becomes yellow or roseate when heated, and colourless again on cooling. The crystals turn yellow and brown-red on exposure to the air, and at 100° black with loss of water; at a higher temperature the acid decomposes, leaving a carbonaceous residue, and yielding a small quantity of an acid sublimate. (Lerch.)

The α-rhodizonates are red, and are produced from the hydrocarboxylates (iii. 189) and from carboxide of potassium by assumption of water and oxygen (Lerch). The *potassium-salt* is obtained by treating the "black mass" of the potassium preparation repeatedly with strong alcohol, then with dilute alcohol, mixed towards the end of the process with a little acetic acid, and finally washing the residue with dilute alcohol. It is at first of an unctuous consistence and light yellowish-red colour, but acquires a crimson colour by exposure to the air, and remains unaltered after drying. It is insoluble in alcohol, dissolves slowly in about 150 pts. of cold water, much more easily in hot water, forming a neutral reddish-yellow solution. (Will.)

Rhodizonate of potassium dried at ordinary temperatures has, according to Will's analysis, the composition $C^5H^2K^2O^6.H^2O$; it gives off its water at 120°—130°, leaving the anhydrous salt $C^5H^2K^2O^6$. The hydrated salt is isomeric with croconate of potassium, $C^5K^2O^5.2H^2O$, but differs from the latter in giving off only half as much water when heated (ii. 111).—The neutral solution scarcely absorbs any oxygen from the air, but if mixed with free potash it quickly turns yellow, absorbs a considerable quantity of oxygen, and then leaves on evaporation a mixture of croconate and oxalate of potassium. The croconic acid is formed from the rhodizonic acid by addition of the elements of water: its formation does not, however, take place immediately, but only on evaporation. The oxalic acid, the proportion of which is not constant, appears to be formed, not from rhodizonic acid, but from a brown substance mixed with it, probably a product of the oxidation of rock-oil not completely removed from the "black mass" by washing with alcohol. (Will.)

Rhodizonate of barium, $C^5H^2Ba''O^6.H^2O$ (vacuum-dried), is obtained, by precipitating the potassium-salt with chloride of barium, as a dark-red precipitate, which becomes dark-brown when dried, acquires a greenish-yellow lustre when pressed, and gives off its water at 100° (Will). The *triplumbic salt*, $C^{10}H^2Pb^3O^{12}.2H^2O$ (vacuum-dried), is obtained, by precipitating the potassium-salt with neutral acetate of lead, as a dark-red flocculent precipitate (the supernatant liquid acquiring an acid reaction), which becomes blue-black when dry, and gives off its water at 100°—120° (Will). Lerch, by precipitating the aqueous acid with neutral acetate of lead, obtained a dark-red basic lead-salt, $C^{10}H^2Pb^3O^{12}.2PbH^2O^2$.—The *triargentic salt*, $C^5HAg^3O^6$, is a purple-red precipitate, metallic-green when dry, slightly soluble in water. (Will.)

β-Rhodizonic acid, $C^{10}H^6O^8$.—This acid is not known in the free state (*i.e.*, as a hydrogen-salt). Its *potassium-salt*, $C^{10}K^6O^8$, discovered by Brodie, remains undissolved when pure carboxide of potassium is treated with absolute alcohol (iv. 696). It is distinguished from the α-rhodizonate by the great facility with which it absorbs oxygen on exposure to air and moisture, and is converted into croconate of potassium:

$$C^{10}K^6O^8 + H^2O + O^3 = 2C^5K^2O^5 + 2KHO \text{ (Brodie).}$$

The α-rhodizonate is probably formed from it in a similar manner by the assumption of a larger quantity of water, thus:

$$C^{10}K^6O^8 + 3H^2O + O^3 = 2C^5H^2K^2O^6 + 2KHO;$$

but this latter reaction has not been actually observed (Will). The conversion of the β-rhodizonate into croconate is not accompanied by the formation of oxalic acid. (Brodie.)

Pure β-rhodizonate of potassium dissolves with pale red colour in dilute acetic acid, and the solution yields, with acetate of barium, a shining red precipitate, which quickly changes colour, even during washing. (Brodie.)

RHODOCHROME. A variety of Kæmmererite from the Ural (iv. 770).

RHODOCHROSITE. Native carbonate of manganese. (See CARBONATES, i. 789.)

RHODONITE. *Siliceous Manganese, Manganese spar, Bustamite, Pajsbergite, Bisilicate of Manganese, rother Mangankiesel, Kieselmangan.*—A mineral consisting mainly of silicate of manganese, but containing also iron, magnesium, and calcium. It usually occurs massive, but sometimes in monoclinic crystals, like angite, having the angle $\infty P : \infty P = 87°7'$, and exhibiting the faces ∞P, $\infty P \infty$, $[\infty P \infty]$, oP. Cleavage perfect parallel to ∞P, imperfect parallel to oP. Hardness = 5·5 to 6·5. Specific gravity = 3·4 to 3·68. It has a vitreous lustre, light brownish-red or flesh-red colour, sometimes greenish or yellowish when impure; streak white. Transparent to opaque. Fracture conchoïdal to uneven. Brittle. Melts to a black bead before the blowpipe, and gives conspicuously with fluxes the reactions of manganese.

Analyses: *a*. From Långhansbyttan in Sweden (Berzelius, Schw. J. xxi. 254).—*b*. St. Marcel in Piedmont (Ebelmin, Ann. Min. [4], vii. 8).—*c*. *Bustamite*, from the Real Minas de Fetela, Mexico: α. by Dumas (Bull. des sc. Nat. 1826, Oct. 163); β. by Ebelmin (*loc. cit.*).—*d*. Algeria: rose-red, granular (Ebelmin).—*e*. *Pajsbergite*, from the Pajsberg iron-mine near Philipstadt in Wermeland, Sweden: rose-red; specific gravity = 3·63. (Igelström, J. pr. Chem. xxiii. 278.)

	a.	*b*.	*c*.		*d*.	*e*.
			α.	β.		
Silica	48·00	46·37	48·90	50·67	45·49	46·46
Manganous oxide	49·04	47·38	36·06	30·73	39·46	41·88
Lime	3·12	5·48	14·57	16·45	4·66	8·13
Ferrous oxide .	. .	. .	0·81	1·31	6·42	3·31
Magnesia	0·22	. .	. .	0·73	2·60	0·91
	100·38	99·23	100·34	99·89	98·63	100·69

These analyses show that—

a. consists of 12 $MnSiO^3.CaSiO^3$
b. „ „ 7 $MnSiO^3.CaSiO^3$
c. „ „ 2 $MnSiO^3.CaSiO^3$
d. „ „ 6 $MnSiO^3.CaSiO^3.FeSiO^3.MgSiO^3$
e. „ „ 24 $MnSiO^3.6CaSiO^3.2FeSiO^3.MgSiO^3$

Fowlerite, from Franklin, New Jersey, where it occurs with Franklinite, is a crystallised manganous silicate resembling the preceding, but likewise containing zinc. Specific gravity = 3·63. The following analyses—*a*. by Hermann (J. pr. Chem. xlvii. 5); *b*. by Rammelsberg (*Mineralchemie*, p. 459)—lead to the formula $7MnSiO^3. 2FeSiO^3. 2CaSiO^3. MgSiO^3. ZnSiO^3$:—

	SiO^2	MnO	FeO	ZnO	CaO	MgO	Loss by ignition.		
a.	46·48	31·52	7·23	5·85	4·50	3·09	1·00	=	99·67
b.	46·70	31·20	8·35	5·10	6·30	2·81	0·28	=	100·74

Manganous silicate is often mixed with manganous carbonate, manganous oxide, or quartz, as in the several varieties of siliceous manganese from Elbingerode in the Hartz, known as *Allagite*, *Photizite*, *Corneous Manganese*, &c. Rhodonite likewise becomes altered by the tendency of manganous oxide to pass to a higher state of oxidation, accompanied by absorption of water, the red colour of the mineral changing to brown or black, and indefinite compounds or mixtures resulting, which may consist either partly of silicates, or wholly of an oxide of manganese. *Marceline* or *Heterocline* from St. Marcel is a mineral of this kind; also *Stratopeite*, a black amorphous mineral of specific gravity 2·64, from the Pajsberg mine in Philipstadt, in which Igelström found 35·43 per cent. silica, 32·41 manganic oxide, 10·37 ferric oxide, 8·04 magnesia, and 13·75 water.

[For analyses of these indefinite varieties of siliceous manganese, see Rammelsberg's *Mineralchemie*, pp. 460—462.]

RHODOPHYLLITE. Syn. with RHODOCHROME.

RHODOTANNIC ACID, or **RHODOXANTHIN.** Tannic acid from the leaves of the *Rhododendron ferrugineum*. (R. Schwarz, Wien. Akad. Ber. ix. 298; Gm. xv. 530.)

RHOMB-SPAR. Syn. with Magnesite or native carbonate of magnesium (i. 787).

RHUBARB. *Rheum*. Many species of rhubarb—*Rheum palmatum*, *Rh. undulatum*, *Rh. compactum*, *Rh. australe*, *Rh. hybridum*, &c.—grow wild on the high lands of Central Asia, and some of them are cultivated in various parts of Europe. The roots are much used for their purgative properties; several kinds occur in commerce, the most esteemed being the Turkey rhubarb. In this country the waved garden rhubarb, *Rheum undulatum*, and the large garden rhubarb, *Rh. hybridum*, are much cultivated for the sake of their juicy stems, which have a pleasant acid taste, and are used for making pastry. The juice of the stems contains oxalic, citric, and malic acids, the latter sometimes in considerable quantity. Dessaignes (J. Pharm. [3] xxv. 23) obtained from a litre of the juice of *Rh. compactum* (after removing the oxalic acid by chloride of calcium), 15 grms. of acid calcic malate; *Rh. Rhaponticum*, on the other hand, yielded only 7 grms.

The root of rhubarb has been made the subject of numerous investigations, the most important of which are those of Schlossberger and Döpping (Ann. Ch. Pharm. l. 196), and of De la Rue and Müller (Chem. Soc. Qu. J. x. 298). Schlossberger and Döpping found, in the alcoholic tincture of rhubarb, a number of substances, which were afterwards found also by De la Rue and Müller in the deposit which separates from the tincture after long standing. These are:—1. *Chrysophanic acid*, which separates to the amount of about 4 per cent. from the alcoholic decoction of the precipitate; 2. *Erythroretin*, contained in the mother-liquor of the chrysophanic acid, and obtained from it by repeated precipitation with ether and solution in alcohol; 3. *Phæoretin*, the portion of the alcoholic decoction which is insoluble in ether; and 4. *Aporetin*, in the portion of the original deposit insoluble in boiling alcohol. (See these several substances.) By exhausting the pulverised root with benzene, or with light coal-tar oil, to extract the chrysophanic acid (which is the best mode of preparing that substance, i. 958), then distilling off the greater part of the solvent, pressing out the liquid from the nearly solid residue, and repeated solution in hot benzene, De la Rue and Müller likewise obtained a reddish-yellow crystalline substance, *emodin*, insoluble in benzene (ii. 485).

For the older investigations of rhubarb-root, which were made chiefly with the view of extracting an active medicinal principle from it, but did not lead to any definite result, see *Handwörterbuch der Chemie*, vi. 819. Schlossberger and Döpping are of opinion that the physiological action of the root cannot be attributed to any one of its constituents in particular.

The ash of the stems and leaves of rhubarb [what species?] has been analysed by Th. Richardson (Jahresb. 1847–48; Tafel C zu S. 1074), with the following results:—

	K^2O	Na^2O	CaO	MgO	SO^3	SiO^2	P^2O^5	$Fe'''PO^4$	$NaCl$		
Stems . .	59·59	0·46	10·04	. .	1·89	2·77	12·83	2·77	8·84	=	99·19
Leaves . .	14·47	31·77	3·95	5·59	9·52	2·33	30·04	2·33	trace	=	100·00

The stems [fresh or dry?] yielded 0·41 per cent., and the leaves 1·23 per cent. ash.

R. Brandes (Jahresb. 1853, p. 581) has examined the inorganic constituents of four kinds of rhubarb-root. A Russian species gave 5·03 per cent. water and 18·2 ash; a Chinese species 8·22 water and 8·82 ash; an older Austrian species, 9·0 water and 5·8 ash; a younger Austrian species (both cultivated at Bilitz), 11·2 water and 5·54 ash.

The ash from 100 pts. of the dried roots contained:—

	Soluble in water.					Insoluble in water.								
	KCl	K^2O	CaO	MgO	SO^3	Fe^2O^3	Al^2O^3	CaO	MgO	MnO	P^2O^5	SiO^2		
Russian	0·196	0·280	0·980	trace	. .	0·100	0·008	8·388	0·244	trace	0·860	0·012	=	11·068
Chinese	0·420	0·215	. .	trace	. .	0·115	0·015	4·095	0·195	trace	0·265	0·025	=	5·345
Austrian, older	0·145	0·840	. .	trace	0·445	0·125	0·060	1·635	0·355	trace	0·755	0·035	=	4·395
Austrian younger	0·020	2·525	. .	trace	0·250	0·140	0·0 5	0·605	0·325	trace	0·370	0·015	=	4·468

Tip (Jahresb. 1854, p. 657) found in 100 parts of rhubarb-root dried at 100° (I. Russian, II. Chinese, III. Root of *Rheum palmatum*, IV. *a* the tap-root, and IV. *b* the branch-roots of *Rh. undulatum*), the following quantites of ash and calcic carbonate:—

	I.	II.	III.	IV. *a*.	IV. *b*.
Ash . . .	17·0	23·0	3·6	11·6	10·0
$CaCO^3$ therein .	15·5	22·3	1·7	11·5	8·4

RHUBARBARIC ACID. }
RHUBARBARIN. } Syn. with CHRYSOPHANIC ACID.

RHUS. *Sumach.* Many species of this genus are very rich in tannic acid, which in *Rhus Coriaria*, *Rh. glabra*, and *Rh. typhina*, exists in all parts of the plant. The tannic acid of the sumachs, like gallotannic acid, yields gallic acid when treated with sulphuric acid. (Stenhouse.)

The leaves of *Rh. copallina* and *Rh. glabra* contain a considerable quantity of acid malate of calcium. *Rh. Metopium* exudes a yellow, emetic, purgative resin; the wood is rich in tannin. *Rh. succedanea* is said by some authorities to yield Chinese wax; according to others, this substance is produced by an insect living on the plant.

The juice of the leaves of *Rhus Toxicodendron* contains gallic acid (Aschoff). Khittel (Jahresb. 1858, p. 530) found in these leaves, besides the usual plant-constituents, an iron-greening tannin and a volatile alkaloïd, which is the poisonous principle. *Rh. venenata* and *Rh. juglandifolia* also contain poisonous principles.

Rh. vernicifera contains a juice which blackens in the air, and is used for the preparation of Japan-varnish; the seeds contain a sebaceous oil. The milky juices of *Rh. Toxicodendron* and *Rh. venenata* likewise blacken on exposure to the air. (Rochleder's *Phytochemie*, pp. 30, 31.)

The air-dried leaves of *Rh. Toxicodendron* yield, according to Khittel, 7·30 per cent., the leaves dried at 100°, 7·91 per cent. ash, containing, in 100 pts.: 25·81 per cent. K^2O, 0·04 Na^2O, 21·59 CaO, 6·45 MgO, 0·49 Al^2O^3, 2·35 Fe^2O^3, 1·54 Cl, 3·98 SO^3, 11·57 P^2O^5, 6·86 SiO^2, 18·43 CO^2 (= 99·11).

The heart-wood of *Rhus pentaphyllum* yields, according to Comaille (J. Pharm. [3] xliii. 269; Jahresb. 1863, p. 616), 0·9 per cent. ash, containing in 100 pts.: 0·25 K^2O and Na^2O, 49·54 CaO, 0·27 MgO, 0·37 Al^2O^3, 8·20 Fe^2O^3, 0·14 Cl, 1·81 SO^3, 2·57 SiO^2, and 36·66 CO^2.

RICINELAÏDAMIDE. $C^{18}H^{35}NO^2$.—A product obtained by the action of alcoholic ammonia on ricinelaïdin. It closely resembles elaïdamide, melts at 91°—93°, and solidifies at 89°. (Rowney, Chem. Gaz. 1855, p. 361.)

RICINELAÏDIC ACID. $C^{18}H^{34}O^3$. *Palmic acid.* (Boudet, Ann. Ch. Pharm. iv. 16.—Playfair, *ibid.* lx. 322.—Bouis, Ann. Ch. Phys. [3], xliv. 82.—Gm. xvii. 135.)—An acid isomeric with ricinoleic acid, produced by the action of nitrous acid on the latter; also by saponifying ricinelaïdin with caustic potash, salting out the resulting soap, and decomposing it with hydrochloric acid. It crystallises in tufts of white silky needles, melting at 50° (Boudet, Bouis), and solidifying to a crystalline mass at 48·5°. Reddens litmus strongly; dissolves easily in alcohol and ether; decomposes alkaline carbonates. Decomposed by distillation, and by heating with soda, in the same manner as ricinoleic acid. The ricinelaïdates of the alkali-metals are soluble in water.—The *barium-salt*, $C^{36}H^{66}Ba''O^6$, obtained by precipitation, is a white powder unctuous to the touch.—The *silver-salt*, $C^{18}H^{33}AgO^3$, is a light white powder, soluble in ammonia, but insoluble in water, alcohol, and ether.

Ricinelaïdate of Ethyl, $C^{20}H^{38}O^3 = C^{18}H^{33}(C^2H^5)O^3$, formed by the action of hydrochloric acid gas on an alcoholic solution of the acid, is a crystalline mass, which melts at 16°, dissolves slightly in cold, very freely in hot alcohol. (Playfair.)

RICINELAÏDIN. $C^{39}H^{72}O^7$?—A solid fatty body produced by the action of nitric peroxide on castor-oil. When purified by washing with water and crystallisation from alcohol, it forms small white nodules melting at 43° (Playfair), at 45° (Bouis), at 62°—66° (Boudet). It solidifies slowly, after remaining pasty for a long time. It is very soluble in alcohol and ether. Caustic potash at the boiling heat converts it into glycerin and ricinelaïdate of potassium. When submitted to dry distillation, it behaves like castor-oil, yielding a dark brown-red, spongy residue, and a distillate of œnanthol (Bertagnini, Ann. Ch. Pharm. lxxxv. 282); and if the œnanthol be driven off by steam, there remains a solid acid, containing 73·8 per cent. carbon and 11·21 hydrogen (Bouis). With care the distillation may be continued to the end without formation of the spongy residue, in which case a large quantity of acrolein and solid hydrocarbons pass over, whilst a little carbon remains behind (Bouis). By distillation with excess of *potash*, ricinelaïdin yields octylic alcohol, sebate of potassium, and two other acids. (Bouis.)

RICINIC ACID. A fatty acid, containing 73·6 per cent. carbon, 9·9 hydrogen, and 16·5 oxygen, said by Bussy and Lecanu to be obtained, together with others, by the saponification, and by the distillation, of castor-oil. (*Gmelin's Handbook*, xvii. 140.)

RICININE. (Tuson, Chem. Soc. J. xvii. 195.)—An alkaloïd contained in the seeds of the castor-oil plant (*Ricinus communis*). The seeds of *Croton Tiglium* contain a similar or perhaps the same base. To prepare it, bruised castor-seeds are exhausted by repeated boiling with water; the decoction is strained, and, after separating the oil as completely as possible, evaporated to an extract, which is boiled with alcohol and filtered. After standing 24 hours, the tincture is separated from the deposited resin, and the alcohol is distilled off. The residue, on standing, deposits crystals of ricinine, which are purified by recrystallisation from alcohol, with the help of charcoal.

Ricinine forms colourless rectangular prisms and laminæ, having a slight taste of bitter almonds, insoluble in water, soluble in alcohol, nearly insoluble in ether and in benzene. When heated, it melts to a colourless liquid, which solidifies in crystalline needles. Sublimes unchanged between two watch-glasses. Contains nitrogen.

When strongly heated on platinum-foil, it burns with a luminous smoky flame. Dissolves in *oil of vitriol* without coloration; the solution is coloured green by chromate of potassium.—Dissolves in *nitric acid* without evolving red fumes, and on evaporation leaves colourless needles, which turn white in water.

Ricinine is insoluble in *water*.—It forms with *hydrochloric acid* a compound, which is decomposed by evaporating the solution.—Its solution mixed with *mercuric chloride*, solidifies after some minutes to a crystalline mass of fine needles.—The hydrochloric acid solution, when evaporated with *chloride of platinum*, yields orange-coloured octahedrons of the double salt.

RICINOLEAMIDE. $C^{18}H^{35}NO^2 = \left.\begin{matrix}C^{18}H^{33}O^2\\H^2\end{matrix}\right\}N$. (Boullay, J. Pharm. [3], v. 329.—Bouis, Ann. Ch. Phys. [3] xliv. 96.)—Produced by saturating an alcoholic solution of castor-oil with ammonia-gas, and leaving it to stand for three or four months, or heating it for a few days in a salt-bath. When purified by crystallisation from alcohol, it forms white crystalline needles, melting at 66°, and solidifying to an opaque brittle mass. It is insoluble in water, soluble in alcohol and ether, and is resolved by acids and alkalis into ammonia and ricinoleic acid.

RICINOLEIC ACID. $C^{18}H^{34}O^3 = \left.\begin{matrix}C^{18}H^{33}O^2\\H\end{matrix}\right\}O$. (Bussy and Lecanu, J. Pharm. xiii. 70.—Saalmüller, Ann. Ch. Pharm. lxiv. 108.—Svanberg and Kolmodin, J. pr. Chem. xlv. 431.—Bouis, Ann. Ch. Phys. [3] xliv. 103, and xlviii. 99.—Petersen, Ann. Ch. Pharm. cxviii. 69.—Gm. xvii. 131.)—A fatty acid produced by saponification of castor-oil and of the oil of *Jatropha Curcas*.

Preparation.—Castor-oil is saponified with potash or soda-ley; the soap is salted out and decomposed by hydrochloric acid; and the oily mixture of ricinoleic acid with a small quantity of solid fatty acids is cooled to −10° or −12° with ½ its volume of alcohol: the solid acids then crystallise out, and are removed. After driving off the alcohol, the ricinoleic acid is digested with excess of lead-oxide, and the lead-salt formed is dissolved in ether, and decomposed by hydrochloric acid and water. The ricinoleic acid, which is left on evaporating the ethereal layer, is purified by dissolving it in aqueous ammonia, precipitating with chloride of barium, and crystallising the barium-salt from alcohol. From the barium-salt the acid is obtained by decomposition with aqueous hydrochloric acid.

Properties.—Ricinoleic acid is a pale wine-yellow syrupy oil, colourless in thin layers. Specific gravity, 0·94 at 15°. Solidifies completely, at − 6° to − 10°, to a granular mass. Inodorous. Has a very disagreeable, persistent, harsh taste. It mixes in all proportions with alcohol and ether. The alcoholic solution has an acid reaction, and decomposes carbonates with effervescence.

Decompositions.—1. Ricinoleic acid, subjected to distillation, yields at first a limpid and afterwards a thick and repulsive-smelling distillate, free from sebacic acid (Saalmüller).—2. It does not absorb oxygen from the air, or even on long exposure to the gas, and does not form carbonic acid (Saalmüller).—3. It absorbs a little sulphurous acid gas, without becoming solid or otherwise altered. (Saalmüller.)

4. By the dry distillation of ricinoleates of the alkali-metals, various products are obtained, according as the neutral salt is distilled alone, or with an excess of alkali:

a. By cautiously distilling the *neutral sodium-salt* until the residue begins to froth up, a distillate of œnanthol (iv. 174) is obtained, the residue containing the sodium-salt of the same acid that is formed by the dry distillation of castor-oil. The sodium-salt and the glyceride of ricinoleic acid are therefore decomposed in the same manner by distillation (Städeler). According to Bouis, the neutral ricinoleates of the alkali-metals yield, by dry distillation, octylic aldehyde (xiii. 187), and a peculiar acid:

$$C^{18}H^{34}O^3 = C^8H^{16}O + C^{10}H^{18}O^2.$$

b. A mixture of potassic or sodic ricinoleate with excess of the caustic alkali froths up when heated, emitting an odour like that of mushrooms; then thickens, gives off at 250° a large quantity of hydrogen gas (no carbonic anhydride or gaseous hydrocarbon) and a volatile oil, and leaves a white spongy residue, consisting of sebate of potassium, together with a neutral oil, which yields a white soap by saponification, and deposits crystals of palmitic acid when cooled (Bouis). The volatile oil is a mixture of methyl-œnanthyl with heptylic or octylic alcohol, or both. (See ALCOHOLS, i. 98; HEPTYLIC ALCOHOL, iii. 145; OCTYLIC ALCOHOL, iv. 170).—According to E. T. Chapman (Chem. Soc. Qu. J. xviii. 290), sometimes the one, sometimes the other alcohol is produced.—The same products are obtained by heating castor-oil with excess of caustic soda. (Bouis.)

Ricinoleates.—Ricinoleic acid is monobasic, the general formula of its salts being

$C^{18}H^{33}MO^2$, or $C^{36}H^{66}M''O^6$. These salts are all soluble in alcohol, most of them also in ether, and crystallisable. They do not alter by keeping, or absorb oxygen from the air.

The *barium-salt*, $C^{36}H^{66}Ba''O^6$, prepared as above (p. 110), crystallises from alcohol in soft scales, slightly soluble in water.—The *strontium-salt*, $C^{36}H^{66}Sr''O^6$, obtained by precipitating the ammonium-salt with chloride of strontium, crystallises from alcohol in small grains.—The *calcium-salt*, $C^{36}H^{66}Ca''O^6$ (at 100°), prepared in like manner, forms scales, which melt at 80° to a yellow mass, brittle and friable after cooling.—The *magnesium-salt*, $C^{36}H^{66}Mg''O^6$, is very soluble in alcohol, and crystallises therefrom in slender needles.—The *zinc-salt* forms small granules.

Lead-salt, $C^{36}H^{66}Pb''O^6$.—The acid heated with excess of lead-oxide loses 2·9 to 3·6 per cent. of water (1 at. = 3·02 per cent.), and forms a solid compound, the ethereal solution of which, evaporated over oil of vitriol, leaves the lead-salt as a transparent crystalline mass, melting at 100° to a light-brown viscid liquid, and solidifying to an easily pulverisable mass. It is very soluble in ether; dissolves in cold, and not much more freely in hot alcohol.—By precipitating ammoniacal ricinoleic acid with neutral acetate of lead, a curdy precipitate of variable composition is obtained. (Saalmüller.)

Silver-salt, $C^{18}H^{33}AgO^3$.—Nitrate of silver throws down from the ammonium-salt a curdy precipitate, which, when treated with alcohol or ether, partially dissolves, but for the most part blackens and remains undissolved. It softens at 100°, melts at higher temperatures to a black mass, and burns with evolution of disagreeably-smelling vapours; dissolves easily in hot alcohol, and slightly in cold alcohol and ether.

Ricinoleate of Ethyl, $C^{20}H^{38}O^3 = C^{18}H^{33}(C\ H^5)O^3$, is prepared by passing hydrochloric acid gas into a solution of the acid in absolute alcohol, and purified by washing with water and carbonate of sodium. It is a yellowish oil, which cannot be distilled without decomposition. (Saalmüller.)

RICINO-MARGARITIC and **RICINO-STEARIC ACIDS.** Names applied by Bussy and Lecanu to certain fatty acids of doubtful composition, obtained from castor-oil: probably mixtures of stearic and palmitic acid. (See CASTOR-OIL, i. 815; also *Gmelin's Handbook*, xvii. 140.)

RIEMANNITE. Syn. with ALLOPHANE (i. 132).

RINMANN'S GREEN. See COBALT-GREEN (i. 1057).

RIOLITE. A selenide of silver, occurring in small lead-grey hexagonal tables, at Tasco in Mexico. Contains, according to Del Rio, 57·7 per cent. silver and 42·34 selenium, whence the formula AgSe. Requires further examination. (Dana, ii. 502.)

RIPIDOLITE. A mineral resembling chlorite in many respects, and allied to it in chemical composition. It occurs in crystals commonly referred to the hexagonal system, with very distinct cleavage parallel to the base. Crystals from the Tyrol exhibit the form of double six-sided pyramids, having the angles of the terminal edges = 132°40′, of the basal edges = 106°30′ (Descloizeaux). According to later observations by Descloizeaux (Ann. Min. [5], xi. 261), however, the crystals have two optic axes inclined to one another at an angle of 20°: hence it would appear probable that the mineral is monoclinic, like chlorite (i. 913).

Hardness = 1—2. Specific gravity = 2·78—2·96. Translucent to nearly transparent, with pearly lustre and green colour, but red across the axis by transmitted light. Streak uncoloured or greenish. Laminæ flexible, not elastic. Before the blowpipe it behaves like chlorite.

Analyses: *a*, *b*. From Greiner in the Zillerthal (v. Kobell, Ann. Ch. Pharm. xl. 244).—*c*. Gumuchdagh, in Asia Minor (Smith, Ann. Min. [4], xviii. 304).—*d*. Mont des Sept-Lacs, Dauphiné (Marignac, Ann. Ch. Phys. [3], xiv. 56).—*e*. Rauris, in the Pinzgau (v. Kobell).—*f*. St. Gotthardt (Varrentrapp, Pogg. Ann. xlviii. 185).—*g*. From the same (Rammelsberg, *ibid.* lxxvii. 414).—*h*. St. Christophe, Dauphiné, (Marignac):—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Silica . . .	26·51	27·32	27·20	27·14	26·66	25·37	25·12	26·88
Alumina . .	21·81	20·69	18·62	19·19	18·90	18·49	22·26	17·51
Ferric oxide .	. .	. .	. .	. .	. .	. .	1·09	
Ferrous oxide	15·00	15·70*	23·21	24·76	28·10†	28·79	23·11	29·76
Magnesia . .	22·83	24·89	17·64	16·78	15·03	17·08	17·41	13·84
Water . . .	12·00	12·00	10·61	11·50	10·69	8·96	10·70	11·33
	98·15	100·60	97·28	99·37	99·38	98·69	99·69	99·32

* With 0·47 manganous oxide.
† With 0·62 " "

These results may be represented by the formula $4M''SiO^3.\ \overset{=}{M}{}^3\overline{\overline{Al}}{}^2O^6.\ 6H^2O$, the numbers of atoms of ferrous oxide and magnesia being in *b.* as 1 : 3, in *d.* as 5 : 6, in *e. f.* as 1 : 1, in *g.* as 5 : 7, and in *h.* as 6 : 5.

Ripidolite occurs also in Scotland.

RISIGALLO. Syn. with REALGAR.

RITTINGERITE. A mineral from the Joachimsthal, occurring in small blackish monoclinic crystals, which behave before the blowpipe like pyrargyrite. According to Breithaupt, it is identical with **xanthocone** (*q.v.*).

RIVULIN. A mucilaginous substance obtained from a freshwater alga, *Rivula tuberosa*. (**Braconnot**, Ann. Ch. Phys. [2] lxx. 206.)

ROBINIC ACID. An acid existing, according to **Reinsch** (Répert. Pharm. [2] xxxix. 198), in the root of the false acacia (*Robinia pseudacacia*). The infusion of the root, evaporated to a syrup, and left in a cool place, deposits rhomboïdal crystals of robinate of ammonium. The free acid is a syrupy mass, which becomes crystalline in contact with absolute alcohol.

ROBINIIN. A yellow colouring matter existing, according to **Kümmell** (N. Br. Arch. xciii. 295), in the wood of *Robinia pseudacacia*, from which it is obtained by precipitating the aqueous decoction with basic acetate of lead, and decomposing the precipitate with sulphydric acid.

ROBININ. $C^{25}H^{30}O^{16}$. (**Zwenger** and **Dronke**, Ann. Ch. Pharm. Suppl. i. 257; Jahresb. 1861, p. 774; 1862, p. 498.)—A yellow substance contained in the blossoms of *Robinia pseudacacia*. To prepare it, the recently gathered flowers are boiled in water, and the decoction is again boiled six or eight times with fresh flowers; it is then evaporated to a syrup, which is repeatedly exhausted with boiling alcohol; the alcohol is distilled off, and the residue is set aside to crystallise; the crystals are pressed and washed with cold alcohol, to remove the greater part of the mother-liquor, and dissolved in boiling water; and neutral acetate of lead is added to the solution, whereby foreign substances are precipitated, while the robinin remains dissolved. The filtrate is freed from lead by sulphydric acid and evaporated, and the robinin is purified by recrystallisation from water.

Robinin thus prepared forms very delicate straw-yellow crystals, having a somewhat silky lustre, and containing $2C^{25}H^{30}O^{16}.11H^2O$. They give off their water (14·45 per cent.) at 100°, leaving anhydrous robinin, which melts to a yellow liquid at 195°, and solidifies to an amorphous mass on cooling. Anhydrous robinin gave by analysis 50·98 per cent. C, and 5·51 H (calc. 51·19 C, 5·10 H, 43·71 O); the hydrate gave 43·50 C and 6·33 H (calc. 43·79 C, 5·98 H, 50·23 O).

Robinin is neutral, tasteless in the solid form, slightly styptic in aqueous solution. Water and alcohol dissolve it slightly in the cold, more freely at the boiling heat; it is insoluble in ether. It dissolves quickly in alkalis and alkaline carbonates, forming golden-yellow solutions; the ammoniacal solution turns brown on standing. The aqueous solution does not precipitate metallic salts; it colours ferric chloride dark-brown or greenish, but does not affect ferrous chloride. The alcoholic solution precipitates neutral and basic acetate of lead. It reduces cupric oxide in a boiling alkaline solution; is not altered by emulsin.

By dry distillation, robinin yields a yellow distillate, containing quercetin in solution. When heated above its melting point, it burns with a smoky flame and a smell of burnt sugar, and leaves charcoal. It is decomposed by concentrated *nitric acid* (with peculiar facility by the fuming acid), with formation of oxalic acid and a large quantity of picric acid. When heated with *dilute acids*, it splits up very readily into quercetin and robinin-sugar:

$$C^{25}H^{30}O^{16} + 2H^2O = C^{13}H^{10}O^6 + 2C^6H^{12}O^6.*$$

100 parts of crystallised robinin yield 37·96 parts of quercetin, dried at 100° (by calculation 38·25 parts).

Robinin-sugar does not crystallise, but is obtained as a sweet brown syrup, which smells like caramel when heated, and yields with nitric acid a large quantity of picric acid, together with traces of oxalic acid. It reduces *cuprate of potassium* in the cold; does not undergo fermentation with beer-yeast.

ROCCELLANILIDE, or *Phenyl-roccellamide*, $C^{29}H^{42}N^2O^2 = \left.\begin{matrix}(C^{17}H^{30}O^2)''\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2$. — When roccellic acid is heated with excess of aniline to 180°—200°, water and aniline distil over, and a black pitchy residue is left, which when drenched with alcohol yields crystals after a few days. These are collected and purified by repeated crystallisation from boiling alcohol, with help of animal charcoal. Roccellanilide thus obtained, forms beautiful colourless laminæ, which melt to a colourless liquid at 53·3°, and solidify partially at 52°. Neutral. At a somewhat elevated temperature, it yields a colourless distillate, without any carbonaceous residue. It is insoluble in water, aqueous ammonia, and hydrochloric acid; not coloured by hypochlorite of sodium. The alcoholic solution does not precipitate alcoholic neutral acetate of lead.

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* It will be observed that the formula of robinin is related to that assigned toquercetin by Zwenger and Dronke (p. 4).

ROCCELLIC ACID. $C^{17}H^{32}O^4 = \left.\begin{matrix}(C^{17}H^{30}O^2)''\\ H^2\end{matrix}\right\} O^2$.—A kind of fatty acid existing in *Roccella tinctoria* and other species of the same genus; also, according to Heeren, in *Lecanora tartarea*. It was discovered in 1830 by Heeren (Schw. J. lix. 346), and has been examined by Liebig (Pogg. Ann. xxi. 31), Schunck (Ann. Ch. Pharm. xxxviii. 459), and Hesse (*ibid.* cxvii. 332).

Preparation.—1. *Roccella tinctoria* is exhausted with aqueous ammonia; the filtrate is precipitated by chloride of calcium; the well-washed precipitate is decomposed by hydrochloric acid; and the acid thus separated is purified by solution in ether (Heeren). The liquid filtered from the roccellate of calcium retains erythric acid (ii. 502) in solution.—2. The lichen is freed from erythric acid by milk of lime; the residue is boiled with dilute hydrochloric acid; the acid solution is removed; and the residue warmed with dilute soda-ley. From the greenish-brown solution, hydrochloric acid throws down green flocks, which must be suspended in water and treated for a short time with chlorine gas, which chiefly removes the green substances. The acid, after being treated with chlorine, is washed with water, and purified by recrystallisation from boiling alcohol, with help of animal charcoal (Hesse). The acid obtained by method 1 may also be purified in this manner, or by passing chlorine into the alkaline solution (Hesse).—3. The lichens are exhausted with ether in a percolator; the ether is distilled off; and the greenish-white crystalline residue is dissolved in the smallest possible quantity of borax-solution, a portion then separating out as the liquid cools. The rest is precipitated by hydrochloric acid, and purified by re-solution in boiling aqueous borax; then, together with the portion of acid first obtained, by recrystallisation from ether, with help of animal charcoal (Hesse). Schunck treats the lichen exhausted with boiling water, and thereby freed from erythric acid [and picroerythrin (ii. 503)], with boiling alcohol; separates the green flocks, which fall down as the tincture cools; and evaporates the filtrate to dryness. From the residue, boiling water extracts a small quantity of picroerythrin; the solution then prepared with cold alcohol deposits, on addition of alcoholic neutral acetate of lead, greenish-white flocks of roccellate of lead, which are decomposed by nitric acid; and the acid thus separated is purified by recrystallisation from boiling alcohol, with help of animal charcoal.

Properties.—Roccellic acid forms delicate, white, rectangular, four-sided plates, having a silvery lustre; from alcohol it separates in short needles. Melts at 132° to a colourless liquid, which solidifies in the crystalline form at about 108°. At a temperature somewhat below 200°, a portion volatilises, while another portion is converted into an anhydride (Hesse). It is tasteless and scentless; the alcoholic solution has an acid reaction. It is perfectly insoluble in water, dissolves in 1·81 pt. of boiling alcohol of specific gravity 0·819, easily in *ether* (Heeren); slightly in warm *benzene*. (Hesse.)

Decompositions.—The acid heated to between 220° and 280° gives off water, turns brown, and leaves roccellic anhydride, $C^{17}H^{30}O^3$ (Hesse). By dry distillation it yields sharp-tasting products similar to those obtained from the fats (Heeren); according to Schunck, a distillate which solidifies in the crystalline form, and after repeated distillation. remains oily, leaving little or no residue. Roccellic acid is but little affected by reagents. It is not decomposed by bromine, sulphuric acid, or hydrochloric acid, and is but slowly oxidised by boiling with hydrochloric acid and chlorate of potassium. When boiled for a long time with fuming nitric acid, it gives off volatile acids having the odour of butyric acid, but does not yield any crystallisable non-volatile acids. It is but slightly altered by fusion with hydrate of potassium; heated with aniline, it forms roccellanilide. (Hesse.)

Roccellates.—Roccellic acid decomposes carbonates. The roccellates of the alkali-metals are soluble in water; the other salts have for the most part the composition $C^{17}H^{30}M''O^4$.—The *barium-salt*, $C^{17}H^{30}Ba''O^4$, obtained by precipitating the ammonium-salt with chloride of barium, is a bulky white precipitate, somewhat soluble in boiling water, insoluble in pure alcohol, but easily soluble in alcohol containing acetic acid.—The *calcium-salt*, $C^{17}H^{30}Ca''O^4.H^2O$, is a white amorphous precipitate, which gives off 48 per cent. water at 160°, and decomposes at a higher temperature, giving off acrolein and a combustible gas (Hesse).—A *basic lead-salt*, $2C^{17}H^{30}Pb''O^4.Pb''H^2O^2.2H^2O$, is obtained by precipitating alcoholic roccellic acid with a warm alcoholic solution of neutral lead-acetate, as a white powder which gives off a small quantity of water at [illegible] then 1·9 per cent. at 125° and melts at a higher temperature (Hesse).—The [illegible] H^4Ag^2 [illegible] obtained by precipitation, is a white amorphous mass, which turns grey on exposure to light. (Hesse.)

[illegible] obtained by passing hydrochloric acid gas into a warm alcoholic solution of the acid, is a pale-yellow oil, having a [illegible] heavier than water, insoluble in water and in aqueous ammonia, and not decomposed either by aqueous or by alcoholic ammonia even after several months' contact, or when heated to [illegible]. It is easily soluble in alcohol, less soluble in ether. (Hesse.)

ROCCELLIC ANHYDRIDE. [illegible].—Obtained by heating roccellic acid to at least 200°, treating the fused brown mass with dilute soda-ley, then agitating it with ether, and evaporating the decanted ethereal solution. It is a colourless or faintly yellow neutral oil, having a fatty odour, makes grease-spots on paper; dissolves sparingly in cold, more easily in hot alcohol and in ether. Boiling soda-ley converts it into roccellic acid. The [illegible] mixed with hydrochloric acid, deposits white flocks [illegible] in alcohol, and remaining, when the alcohol is evaporated, as a semi-crystalline acid oil having a burning taste: probably a mixture of roccellic and roccellamic acids. (Hesse.)

ROCCELLIC ETHER. ([illegible])

ROCCELLININ. [illegible] (Stenhouse, Ann. Ch. Pharm. lxviii. 69.)—A crystalline substance obtained, together with β-orsellic acid (iv. 235), from *Roccella tinctoria*. To prepare it, the gelatinous mass obtained by precipitating the lime-extract of the lichen with hydrochloric acid is boiled with alcohol, whereby the β-orsellic acid is transformed into orsellinate of ethyl (iv. 236), while the roccellinin remains unaltered. The product is treated with boiling water, which dissolves out all the ethylic orsellinate, leaving the roccellinin undissolved.

Roccellinin crystallises from boiling alcohol in silky needles, nearly insoluble in cold alcohol and ether. It gives by analysis 62·44—62·67 per cent. carbon, and 4·65—4·90 hydrogen, the formula [illegible] requiring 62·8 C., 4·7 H. and 32·5 O. It is easily dissolved by ammonia and the fixed alkalis: the solutions do dot become coloured on exposure to the air. It is not attacked by baryta or by boiling potash. It does not precipitate metallic solutions. Hot nitric acid converts it into oxalic acid.

ROCHELLE-SALT. Sodio-potassic tartrate. (See TARTARIC ACID.)

ROCHLANDITE. Syn. with SERPENTINE.

ROCK-CORK. A variety of asbestos (i. 415).

ROCK-CRYSTAL. Pure crystallised silica. (See QUARTZ.)

ROCK-MILK, or *Agaric Mineral.* A loose friable variety of limestone (iii. 696).

ROCK-SALT. See SODIUM, CHLORIDE OF.

ROCK-SOAP. A variety of bole.

RŒMERITE. A hydrated ferroso-ferric sulphate, occurring on the Rammelsberg, near Goslar, in monoclinic crystals, accompanied and interpenetrated by ferrous and ferric sulphates. (*Rammelsberg's Mineralchemie*, p. 292.)

RŒSSLERITE. A hydrated arsenate of magnesium, occurring, together with pharmacolite and cobalt-bloom, in the cupriferous shale of Biber, near Hanau. It forms thin fibrous or laminar plates, or dentiform and vermicular masses, apparently cleavable in one direction; hardness (of the unaltered mineral) = 2 to 3. Translucent to transparent, colourless or white, with vitreous lustre. On exposure to the air it becomes opaque, dull, and less hard, apparently from loss of water. Before the blowpipe it gives up its water and melts to a white enamel. Dissolves easily in hydrochloric acid (Blum, Jahresb. 1861, p. 1031). Contains, according to Delffs, 40·16 As^2O^5, 14·22 MgO, with trace of cobalt, and 45·62 water (= 100), whence the formula $2Mg''O.As^2O^5.15H^2O$.

RŒTTISITE. A mineral, consisting essentially of hydrated nickel-silicate, occurring, together with conarite (hydrated nickel-phosphate), in the Hans-Georg mine near Röttis, in the Saxon Voigtland. It forms thick lenticular and wedge-shaped masses, sometimes weighing several pounds; is of an emerald-green colour, rarely passing into apple-green; usually dull and opaque, but translucent on the edges; sometimes brittle, and splits with moderate facility. Fracture conchoïdal to earthy. Streak, dark apple-green. Hardness = 2 to 3. Specific gravity = 2·356 to 2·370. A. Winckler found in lumps translucent on the edges:

NiO	CoO	CuO	Fe^2O^3	Al^2O^3	SiO^2	P^2O^5	As^2O^5	SO^3	H^2O		
35·87	0·67	0·40	0·81	4·68	39·15	2·70	0·80	trace	11·17	=	95·55

Hence the mineral appears to consist essentially of $3(3Ni''O.SiO^2).4H^2O$. (Breithaupt, Jahresb. 1859, p. 791.)

ROMANZOVITE. A brownish lime-garnet from Kimito in Finland.

ROMEINE, or **ROMEITE.** A mineral found at St. Marcel in Piedmont, in groups of minute crystals in the gangue which accompanies manganese. The crystals are dimetric octahedrons, having the basal angle = 110° 50′—111° 20′, and the angle over the summit 68° 10′—69° 10′ (Dufrénoy). It scratches glass. Specific gravity in grains = 4·714; in powder = 4·675. Colour, hyacinth or honey-yellow. Contains 15·82 per cent. oxygen, 62·18 antimony, 1·31 iron, 1·21 manganous oxide, 16·29 lime, 0·96 soluble silica, and 1·90 insoluble silica = 99·67 (or 40·79 Sb^2O^5, 36·82 Sb^2O^3, 1·70 FeO, 1·21 MnO); and may be represented by the formula $3M''O.Sb^2O^3.Sb^2O^5$. (Damour, Ann. Min. [3] xx. 247; [5] iii. 179.)

ROSANILINE. *Aniline-red.* See PHENYLAMINES (iv 468). Nitrous acid converts it into rosolic acid. (Wanklyn and Caro, p. 117.)

Hydrocyan-rosaniline, $C^{21}H^{20}N^4 = C^{20}H^{19}N^3.HCy$. (Hugo Müller, Zeitschr. Ch. Pharm 1866.)—A base produced by addition of the elements of hydrocyanic acid to rosaniline, analogous therefore in composition to hydrocyanharmaline (iii. 8). It has a great resemblance to leucaniline, the base formed from rosaniline by addition of hydrogen (iii. 574). It is prepared by treating a finely pulverised rosaniline-salt with alcohol and cyanide of potassium (the latter being added in the proportion of about ⅛, if acetate of rosaniline is used); the resulting yellowish white powder is washed on a filter with alcohol, then dissolved in dilute hydrochloric acid; the solution is warmed and mixed with dilute alcohol; and the base is precipitated by ammonia, mixed with a little cyanide of potassium or hydrocyanic acid, in case the solution should still exhibit a red colour from unaltered rosaniline. A white or yellowish-white bulky precipitate is thus obtained, which becomes crystalline after a while, and then quickly settles down. If it is coloured, it may be purified by resolution and reprecipitation; or the hydrochloric acid solution may be decolorised by treatment with animal charcoal.

Hydrocyan-rosaniline precipitated from the aqueous hydrochlorate by ammonia, forms a dazzling white opaque crystalline powder. From a warm alcoholic solution, it separates in small transparent monoclinic crystals, having a splendid diamond lustre. Alkalis added to a very dilute aqueous solution of one of its salts, separate the base either as a milky turbidity or a curdy precipitate resembling chloride of silver. It is permanent in the dark, but becomes rose-red on the surface when exposed to sunlight. It is decomposed by fusion with potash, apparently with reproduction of rosaniline.

Hydrocyan-rosaniline dissolves very easily in hydrochloric, nitric, and sulphuric acids, forming colourless crystallisable salts. The *hydrochlorate* separates from a very concentrated solution, in large apparently monoclinic crystals, permanent in the air, and very soluble in alcohol. The *nitrate* and *sulphate* are also very soluble, but more difficult to crystallise, the solutions having a great tendency to dry up to gummy masses. The solution of the hydrochlorate is not precipitated by chloride of platinum, but on evaporation, the *chloroplatinate* separates as a heavy resinous body. A solution of potassic *picrate* forms, even in very dilute solutions of the salts, a yellow flocculent precipitate, which at a gentle heat cakes together to a dark-yellow resin.

ROSE, OIL OF. A volatile oil, extracted chiefly in Persia, India, and the State of Tunis, from several species of very odoriferous roses, especially *Rosa centifolia*, *R. damascena*, *R. moschata*. It is a thick yellow liquid, solidifying at low temperatures to a buttery mass of transparent, colourless, shining laminæ, which does not liquefy completely again below 28°—30°. The scent of the oil is very fragrant when much diluted; but in the concentrated state it causes headache. The oil is a mixture, in variable proportions, of a camphor or stearoptene, and an oxygenated oil which has not been analysed. Specific gravity of the crude oil = 0·87 (Chardin, Ann. Ch Pharm. vii. 154); 0·8912 at 15·5° (Gladstone and Dale, Chem. Soc. Qu. J. xvii. 1). Index of refraction at 25° = 1·4567 for the line A, 1·4627 for D, 1·4835 for H. Molecular rotatory power = 7°. (Gladstone and Dale.)

Rose-camphor is very slightly soluble in alcohol, but very freely in ether and essential oils. It forms laminæ, melting at 35°, and boiling between 280° and 300°. It is a hydrocarbon having the composition of ethylene (Saussure, Blanchet, and Sell). It is soluble in caustic potash and acetic acid; very slightly attacked by hydrochloric and nitric acid.

Oil of roses is often adulterated with oil of geranium. According to Guibourt (J. Pharm. xv. 345), the adulteration may be detected, either by means of strong *sulphuric acid*, which does not impair the purity and sweetness of rose-oil, but developes in geranium-oil a strong disagreeable odour, even with very small quantities; or by exposing the oil to *iodine-vapour*, which does not alter the colour of rose-oil, but colours geranium-oil a very deep brown; or by exposing it to *nitrous acid*, which colours rose-oil deep yellow, and geranium-oil apple-green.

ROSEINE. Syn. with Rosaniline (iv. 468).—D. S. Price (Rep. Pat. Invent. 1860, p. 159; Jahresb. 1859, p. 760) applies the term especially to the red dye obtained by treating sulphate of aniline with peroxide of lead.

ROSELITE. An arsenate of cobalt, occurring in small quantity, on quartz, at Schneeberg in Saxony, in trimetric crystals, having the angle $\infty P : \infty P = 132° 48'$; $oP : \bar{P}\infty = 158° 2'$. Cleavage distinct and brilliant, parallel to $\infty \bar{P}\infty$. Hardness = 3. Colour deep rose-red. (Levy, *Dana's Mineralogy*, ii. 417.)

ROSELLAN, or **ROSITE.** A variety of anorthite, from Aker in Södermanland, Sweden, having a rose-red colour and granular structure. When heated, it gives off water and becomes colourless; melts easily before the blowpipe. Contains, according to Svanberg, 44·90 per cent. silica, 34·50 alumina, 0·69 ferric oxide, 0·19 manganic oxide, 3·59 lime, 2·45 magnesia, 6·63 potash, and 6·53 water. (*Rammelsberg's Mineralchemie*, p. 592.)

ROSEMARY, OIL OF. Obtained by distilling the fresh leaves and flowers of *Rosmarinus officinalis* with water. It is transparent, colourless or yellow, of specific gravity 0·88 to 0·91 (Zeller), 0·9080 at 15·5° (Gladstone and Dale). Boils at 165°—168° (Kane); neutral; has a camphorous taste, and the odour of the plant. Index of refraction at 16·5° = 1·4632 for A; 1·4688 for D; 1·4867 for H. Optical rotatory power = —17° (Gladstone and Dale). According to Lallemand, on the contrary, it is dextrorotatory.

Oil of rosemary is blackened by strong sulphuric acid; the mixture saturated with lime yields the calcium-salt of a peculiar acid (Unverdorben). The mixture of rosemary-oil and sulphuric acid yields by distillation an empyreumatic oil (Kane's *rosmarine*) having the alliaceous odour of mesitylene, a specific gravity of 0·807, boiling at 173°, and isomeric with turpentine-oil. (See *Gmelin's Handbook*, xiv. 396.)

According to Lallemand (Ann. Ch. Phys. [3] lvii. 404), oil of rosemary may be separated by fractional distillation into two oils, one boiling at 165°, the other between 200° and 210°.—*a.* The former is a mobile hydrocarbon, which turns the plane of polarisation to the left; it unites with *hydrochloric acid*, the combination being attended with rise of temperature, and forms a compound, which remains liquid if left to itself, but when treated with nitric acid, yields a considerable quantity of a crystalline hydrochlorate, apparently identical with hydrochlorate of turpentine-oil, or artificial camphor, $C^{10}H^{16}.HCl$. The same oil quickly absorbs moist oxygen in sunshine, forming crystals, which are similar to those produced in like manner from oil of turpentine, but disappear if subjected to the further action of oxygen, yielding a brown acid soluble in water.

b. The portion boiling between 200° and 210° deposits, at low temperatures, a large quantity of camphor, resembling common camphor in all respects, excepting that it has rather less dextrorotatory power. An additional quantity of it may be obtained by treating the mother-liquor with dilute nitric acid.

ROSENITE. Syn. with Plagionite.

ROSEO-CHROMIC SALTS. See Chromium (i. 951).

ROSEO-COBALTIC SALTS. See Cobalt-bases, Ammoniacal (i. 1052). For Braun's view of the constitution of these and other ammoniacal cobalt-compounds, see Ann. Ch. Pharm. cxxxii. 33; Jahresb. 1864, p. 273.

ROSE QUARTZ. See Quartz (p. 1).

ROSETTE-COPPER. See Copper (ii. 33).

ROSEWOOD, OIL OF. *Oleum ligni rhodii.*—A volatile oil obtained from rosewood (*Convolvulus scoparius*), by distillation with water. It is pale-yellow, somewhat viscid, and consists, to about $\frac{4}{5}$, of a hydrocarbon, $C^{10}H^{16}$, which boils at 249°, and smells like roses and sandalwood. Specific gravity of the crude oil = 0·9064 at 15·5°. Index of refraction at 17° = 1·4843 for A; 1·4903 for D; 1·5113 for H. Optical rotatory power = —16° (Gladstone and Dale). Rosewood-oil is sometimes used for adulterating oil of roses, which thereby loses its buttery consistence.

ROSITE. Syn. with Rosellan.

ROSOLIC ACID. A compound produced by the oxidation of phenol in presence of alkalis. It was discovered by Runge (Pogg. Ann. xxxi. 70), amongst the products obtained by treating coal-tar oil with milk of lime. When the mixture of phenol, rosolic acid and brunolic acid (i. 684), thus obtained, is distilled with water, phenol passes over, and a pitchy residue is left, containing rosolic and brunolic acids. This residue, dissolved in alcohol and mixed with milk of lime, yields a rose-coloured solution of calcic rosolate, and a brown precipitate of calcic brunolate. The solution evaporated to a syrup, and mixed with a third of its volume of alcohol, deposits, after a few days, rose-coloured crystals of calcic rosolate, from which the rosolic acid may be separated by acetic acid (Runge). To obtain the rosolic acid pure, the treatment with lime and alcohol, and the decomposition of the calcium-salt by acetic acid, must be repeated several times; and finally, the alcoholic solution of the acid, which is still not quite free from lime, must be mixed with a little hydrochloric acid, and diluted with a large quantity of water: the rosolic acid then separates out pure. (Hugo Müller, Chem. Soc. Qu. J. xi. 1: see also Tschelnitz. J. pr. Chem. lxxi. 416; Jahresb. 1857, p. 447.)

Rosolic acid is more easily prepared by heating phenol with certain metallic oxides in presence of an alkali. R. Angus Smith (Chem. Gaz. p. 20), obtained it by heating phenol with soda and peroxide of manganese; but it is difficult to free the product from the manganate of sodium formed at the same time. An easier process is that given by Jourdin (Rép. Chim. app. iii. 217), who uses mercuric oxide instead of manganic peroxide. The action, which takes place below 150°, is complete in about ten minutes, and the solution decanted from the reduced mercury contains pure rosolate of sodium. Rosolic acid is likewise produced, with evolution of hydrochloric acid, by heating phenol with mercuric chloride (Jourdin); also, according to Schützenberger and Sengenwald (iv. 394), by heating di-iodophenol in contact with the air.*

According to Wanklyn and Caro, rosolic acid is closely related to rosaniline (iv. 468), and may be produced by adding a solution of a nitrite to any salt of rosaniline, and boiling the solution. During the boiling, a copious evolution of nitrogen occurs, and the rosolic acid gradually separates out in the form of a pitch, with a cantharides-like lustre. The reaction probably takes place by two stages, as follows:—

$$\underset{\text{Rosaniline.}}{C^{20}H^{19}N^{3}} + 3HNO^{2} = \underset{\text{Azorosaniline.}}{C^{20}(H^{10}N'''^{3})N^{3}} + 6H^{2}O.$$

$$\underset{\text{Azorosaniline.}}{C^{20}H^{10}N^{6}} + 4H^{2}O = \underset{\text{Rosolic acid.}}{C^{20}H^{18}O^{4}} + 3N^{2}$$

Rosolic acid is a dark-coloured amorphous substance, having a greenish lustre, and yielding a red powder; in thin films it exhibits a red colour by transmitted light. It bakes together at about 60°, and melts in boiling water to a dark-green, nearly black liquid. It is not volatile, and not easily combustible. It dissolves readily, with brownish-yellow colour, in alcohol and ether; also in phenol, in wood-creosote, in strong acetic, hydrochloric, and sulphuric acids, and is not quite insoluble in water; chloroform, benzene, and sulphide of carbon do not dissolve it (Hugo Müller). Its composition has not been fixed with certainty. According to the mean of Müller's analyses, rosolic acid dried over oil of vitriol contains 75·92 per cent. carbon and 5·83 hydrogen, agreeing nearly with the empirical formula $C^{23}H^{22}O^{4}$, which requires 76·27 C, 6·05 H, and 17·68 O. Angus Smith proposed the formula $C^{12}H^{12}O^{3}$ (requiring 70·6 per cent. carbon), and Dusart (Rép. Chim. app. i. 207), from his own analysis (not given), deduces the formula $C^{6}H^{6}O^{2}$, requiring 65·4 per cent. carbon. According to Wanklyn and Caro, the true formula is probably $C^{20}H^{18}O^{4}$ (*vid. sup.*).

Rosolic acid distilled over excess of soda-lime yields phenol, a portion, however, suffering further decomposition (Dusart). According to Wanklyn and Caro, it yields phenol by distillation *per se.* It is easily attacked in alcoholic solution by chlorine and bromine, also by nitric acid when heated, forming a light-yellow substance, which dissolves in caustic alkalis, but not with red colour. It is not acted upon by a solution of glucose in caustic potash (Müller), and is not decolorised by sulphurous acid (Dusart). When boiled with aniline and little benzoic acid, it forms a splendid and very permanent blue dye, the reaction not being attended with evolution of ammonia, but apparently with separation of water. (Wanklyn and Caro.)

Rosolates.—Rosolic acid is a very weak acid, weaker even than carbonic acid. It unites with ammonia, the fixed alkalis, and the alkaline earths, forming dark-red compounds, soluble in water and alcohol, and very easily decomposed by exposure to light and air, being partly converted into carbonates, and losing their colour.—The carmine-red solution of rosolic acid in alkalis is decolorised by boiling with zinc-powder, but the colour is restored by addition of ferricyanide of potassium. (Wanklyn and Caro.)

The *calcium-salt* separates on carefully evaporating its solution in a vacuum over lime, as a granular or crystalline powder, which when pressed resembles carthamin.—The *magnesium-salt* is the most stable of the rosolates. The soluble rosolates do not form precipitates with the salts of the heavy metals, not even with basic acetate of lead; neither does rosolic acid combine with alumina. (H. Müller.)

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* Communication from Prof. Wanklyn.

ROTHOFFKITE. A name of garnet.

ROTTLERA. The fruit of *Rottlera tinctoria*, a tree growing in all parts of India, is covered with stellate hairs and glands, which, when brushed off, form a brick-red sandy powder, used in India as a dye, and lately introduced into medicine, under the name of *Kamala*, as a remedy for tapeworm. It has an aromatic odour, is but slowly wetted by water, and yields but little to boiling water, colouring it only a pale-yellow; but alkaline carbonates and caustic alkalis, especially the latter, extract the colouring matter, forming deep red solutions. The extract prepared with soda imparts to silk a fine and durable fiery-orange colour, without further addition or the use of mordants; with cotton, on the other hand, it does not produce a good colour. The natural dye-stuff contains 3·49 per cent. water, 78·19 resinous colouring-matters, 7·34 albuminous substances, 7·14 cellulose, and 3·84 ash, besides small quantities of volatile oil and a volatile colouring matter. (The liquid distilled from the alcoholic extract has a yellow colour, and the odour of the original substance). The concentrated ethereal extract of the colouring matter deposits a yellow crystalline substance called *Rottlerin* (vid. inf.). The extract prepared with boiling alcohol deposits, on cooling, non-crystalline flocks of a substance having the composition of $C^{30}H^{34}O^{4}$. It may be obtained, nearly colourless, by repeated solution and separation; is sparingly soluble in ether and in cold alcohol, insoluble in water; not precipitated by lead- or silver-salts. The alcoholic solution separated from these flocks leaves a dark-red resin, $C^{30}H^{30}O^{7}$, soluble in all proportions in alcohol and ether, insoluble in water, melting at 100°, and forming with acetate of lead, a deep orange-coloured precipitate of variable composition. (**Anderson**, Edinb. New Phil. Journ. new series, i. 300; Jahresb. 1855, p. 669.)

G. **Leube**, Jun. (Vierteljahrschr. pr. Pharm. ix. 321; Jahresb. 1860, p. 562) has also examined the red colouring matter of *Rottlera tinctoria*, but with very different [and doubtful] results, not having even succeeded in preparing the crystallised substance rottlerin. He found in the deep red powder 47·6 per cent. resinous substances, 19·7 of other constituents extractable by solvents (extractive matter, oxalic acid, albumin, ulmic acid, and inorganic salts), 7·7 fibrin, and 25·0 [insoluble] mineral substances. The resinous substance extracted by ether was resolved by treatment with cold alcohol into two resins, one easily soluble, the other sparingly soluble, in that liquid. The former, melting at 80°, contains $C^{15}H^{18}O^{4}$; the latter, melting at 191°, contains $C^{8}H^{12}O^{5}$. Both are brittle, reddish-yellow, dissolve with fine red colour in cold potash-ley, alkaline carbonates, and ammonia, and are separated therefrom by acids without alteration; they are not altered by boiling with dilute sulphuric acid, but nitric acid decomposes them, with formation of oxalic acid. The ash, amounting to 28·85 per cent. of the red substance, was found to contain 0·9 per cent. potash and soda, 0·2 magnesia, 4·1 lime, 0·7 manganic oxide, 8·5 ferric oxide, 1·2 soluble silica, 83·8 insoluble silica [it was probably mixed with sand], and traces of chlorine and sulphuric acid.

ROTTLERIN. $C^{11}H^{10}O^{3}$. (**Anderson**, *loc. cit.*)—This substance separates from the ethereal extract of the colouring matter of *Rottlera tinctoria*, in yellow silky crystals, which are insoluble in water, sparingly soluble in cold, more easily in boiling alcohol, melt when heated, and then decompose. It dissolves in alkalis with deep red colour. Its alcoholic solution is not precipitated by acetate of lead. With bromine it forms a colourless substitution-product: with nitric acid, first a yellow resin, and then oxalic acid; with cold concentrated sulphuric acid, a yellow solution, which when heated becomes darker and gives off sulphurous acid.

ROUCOU. Syn. with Annotto (i. 307).

RUBEANHYDRIC ACID. The name given by Berzelius to the compound $C^{2}N^{2}H^{4}S^{2}$ or $Cy^{2}.2H^{2}S$. (See Cyanogen, Sulphydrates of, ii. 285.)

RUBELLAN. An altered biotite (iii. 1013), occurring in small hexagonal forms, of a red colour, in a kind of wacke. (**Dana**, ii. 226.)

RUBELLITE. Red tourmaline.

RUBERYTHRIC ACID. A yellow substance existing, according to **Rochleder** (Ann. Ch. Pharm. lxxx. 321; lxxxii. 205), in madder-root. To prepare it, the aqueous decoction of the root is precipitated by neutral acetate of lead; the precipitate (which serves for the preparation of alizarin and purpurin), is collected on a filter; and the filtrate is mixed with basic acetate of lead, not in excess, which throws down a dark, flesh-coloured, nearly brick-red precipitate, containing ruberythric and rubichloric acids, with small quantities of citric and phosphoric acids. This precipitate is suspended in water, and decomposed by sulphydric acid; the solution, chiefly containing rubichloric acid, is filtered from the sulphide of lead; and the ruberythric acid, which remains attached to this lead-precipitate, is extracted from it, after washing for a short time, by boiling with alcohol. The alcoholic solution evaporated to one-third, then mixed with water and a small quantity of baryta-water, deposits a scanty white precipitate; and the filtrate, treated with a larger quantity of baryta-water, yields ruberythrate of barium in dark cherry-red flocks. These are collected and dissolved in dilute acetic acid; and the solution is nearly neutralised with ammonia, and precipitated by basic acetate of lead, whereby a cinnabar-coloured lead-salt is obtained, which must be washed with dilute alcohol, and decomposed under alcohol by sulphydric acid. The liquid heated to the boiling-point with the sulphide of lead, then filtered hot and evaporated, deposits light-yellow crystals of ruberythric acid, which may be purified by pressure and recrystallisation from a small quantity of boiling water.—25lbs. madder yield 1 gramme of the acid; Levantine more than European madder.

Ruberythric acid forms yellow prisms having a silky lustre. It has a faint taste; dissolves sparingly in cold, easily in hot water; with gold-yellow colour in alcohol and ether, with blood-red colour in aqueous alkalis; forms red precipitates with baryta-water, with alum-solution after addition of ammonia, and with basic acetate of lead, after addition of a little alcohol. Boiling aqueous ferric chloride dissolves it, forming a dark brown-red solution, which is precipitated by alcohol.

Ruberythric acid contains, according to Rochleder's analysis, 54·48 per cent. carbon and 5·16 hydrogen, agreeing nearly with the formula $C^{36}H^{40}O^{20}$ (calc. 54·54 C, 5·05 H, and 40·41 O), or with $C^{36}H^{42}O^{21}$ (calc. 54·64 C, 5·04 H, and 40·32 O). The percentage composition is nearly the same as that of rubian (p. 123); in fact, Rochleder regards rubian as merely impure ruberythric acid. Schunck, on the contrary, did not find ruberythric acid in madder, and is of opinion that, in the preparation above described, products of the decomposition of rubian must have been obtained.

Ruberythric acid heated in aqueous solution with hydrochloric acid is resolved into alizarin and glucose. The reaction may be represented, according to Rochleder, by either of the equations:

$$\underset{\text{Ruberythric acid.}}{C^{36}H^{40}O^{20}} = \underset{\text{Alizarin.}}{3C^{10}H^{6}O^{3}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}} + 5H^{2}O.$$

or:

$$3C^{36}H^{42}O^{21} = 12C^{10}H^{6}O^{3} + 8C^{6}H^{12}O^{6} + 9H^{2}O.$$

The aqueous solution boiled with alkalis also deposits alizarin on addition of an acid. (Rochleder.)

RUBIA. See MADDER (iii. 740).

RUBIACIC ACID. An acid produced, according to Schunck (Ann. Ch. Pharm. lxvi. 201; lxxxvii. 344), by boiling rubiacin or rubiafin, or the brown flocks thrown down by hydrochloric acid from spent madder-liquor, with ferric nitrate or chloride. The resulting brown-red solution, mixed with hydrochloric acid, deposits brown flocks of impure rubiacic acid, which may be purified by solution in boiling aqueous carbonate of potassium, and reprecipitation with an acid. It is a lemon-yellow amorphous powder, slightly soluble in boiling water, and converted by sulphuric acid, first into rubiacin, then into rubiafin. Contains, according to Schunck, 57·6 per cent. C, 2·9 H, and 39 5 O, which he represents by the formula $C^{32}H^{9}O^{17}$ or $C^{32}H^{18}O^{17}$, requiring 57·0 C, 2·7H, and 40·3 O. The potassium-salt forms brick-red needles or prisms, containing 13·04 per cent. potash, the formula $C^{32}H^{8}KO^{17}$ requiring 12·58 per cent.

RUBIACIN. *Madder-orange. Krapp-orange.* (Runge, J. pr. Chem. v. 367; Robiquet, Ann. Ch. Phys. lxiii. 311; Higgin, Phil. Mag. [3] xxxiii. 232; Schunck, *Gmelin's Handbook*, xvi. 47.)—A yellow, crystallisable colouring-matter, discovered by Runge. It exists in madder-root, probably as a calcium-compound, from which it separates as the extract turns sour. It is also produced by the action of alkaline hydrosulphates on rubiacic acid (Schunck), and by heating Higgins' xanthin (*q. v.*) with strong sulphuric acid, and by the spontaneous decomposition of that substance which takes place when an aqueous extract of madder is left to itself. Rubiacin is found partly in the precipitate produced by acids in the decoction of madder, partly in the residue left after exhausting the root with water, and may be obtained in the pure state by conversion into rubiacic acid and subsequent reduction of that compound. (Schunck). It may also be prepared from the madder-liquor of the dye-houses, by mixing the liquid with hydrochloric acid, treating the resulting precipitate with boiling alcohol, redissolving the orange-yellow powder which separates on cooling, in boiling alcohol, and adding stannous oxide to the solution. The hot filtrate deposits rubiacin, or cooling, in splendid light-yellow plates and needles, having a strong reddish-green lustre like iodide of lead. When heated, it sublimes completely in yellow scales (Schunck). It is slightly soluble in boiling water, more soluble in boiling alcohol. It contains 67·1 per cent. carbon and 4·0 hydrogen, whence Schunck deduces the formula $C^{32}H^{22}O^{10}$ (calc. 67·8 C, 3·9 H, 28·3 O).

Rubiacin dissolves in strong sulphuric acid, forming a yellow liquid, which may be heated without decomposition. Strong nitric acid attacks it at the boiling heat. It dissolves in ferric chloride or nitrate, forming a brown solution, which on addition of an acid, turns yellow and deposits flocks of rubiacic acid. It dissolves in alkalis, forming purple solutions, from which acids throw down yellow flocks. The ammoniacal solution forms dingy-red precipitates with the chlorides of barium and calcium.

Hydrate of aluminium introduced into an alcoholic solution of rubiacin acquires an orange tint, and decolorises the liquid. The alumina-precipitate dissolves easily in caustic potash, forming a purple solution. A piece of mordanted calico is scarcely coloured by rubiacin suspended in boiling water. (Schunck.)

RUBIADIN. $C^{16}H^{14}O^{5}$. (Schunck, Phil. Mag. [4] v. 410, 495; xii. 200, 270.)—A body produced, together with glucose, by the action of alkalis on rubiacin (respecting its mode of formation, see MADDER, iii. 746); also in the decomposition of rubihydran or rubidehydran by dilute hydrochloric or sulphuric acid.

Preparation: 1. When rubian is boiled for some time with caustic soda, a precipitate is formed, consisting chiefly of the soda-compound of alizarin (i. 114); and the alkaline mother-liquor, mixed with dilute sulphuric acid and a large quantity of water, deposits yellow flocks containing alizarin, rubiretin, verantin, and rubiadin, while glucose remains in solution. The flocks are treated with boiling alcohol, which dissolves them, leaving only a brown substance formed from the sugar; and the filtered liquid is treated with acetate of aluminium, whereby the alumina-compound of alizarin is precipitated, together with a small quantity of verantin.

The mother-liquor is then mixed with acetate of lead, which throws down rubiretin and verantin as a brownish-purple precipitate (see RUBIRETIN), while rubiadin remains in solution, still mixed, however, with a small quantity of rubiretin. By precipitating the solution with a large quantity of water, dissolving the yellow flocks thereby obtained in the exact quantity of boiling alcohol required, and digesting with hydrate of lead (or stannous hydrate), the rubiretin is removed, and the hot-filtered solution deposits rubiadin on cooling; an additional quantity of that substance, but in an impure state, is obtained by evaporating the mother-liquor. This latter product may be purified by sublimation.

2. An aqueous solution of rubihydran (p. 131) is boiled with hydrochloric or sulphuric acid till it becomes colourless, and no longer deposits yellow flocks or a brown resin. These flocks are a mixture of rubiretin, verantin, and rubiadin, with a small quantity of alizarin; the alizarin may be separated by acetate of aluminium, and then the rubiadin, in the same manner as from the mixture of these bodies obtained by the first method.

Rubiadin crystallises in yellow needles, or in rectangular plates, which are sublimable, insoluble in water, more soluble in alcohol than rubianin. Strong sulphuric acid dissolves it, with yellow colour; aqueous ammonia and carbonate of sodium dissolve it at the boiling heat, with blood-red colour. It is precipitated by chloride of barium, chloride of calcium, and cupric acetate, not by acetate of of lead; does not dissolve in ferric chloride.

Rubiadin gives by analysis 69·6 per cent. carbon and 5·1 hydrogen, whence Schunck deduces the formula $C^{32}H^{13}O^{9}$ (calc. 69·3 C, 4·7 H, and 26·0 O). It is more probably $C^{32}H^{14}O^{10}$ or $C^{16}H^{14}O^{5}$.

Chlororubiadin, $C^{16}H^{13}ClO^{5}$. (Schunck, Phil. Mag. [4] xii. 270.)—Produced by boiling chlororubian (p. 124), with dilute sulphuric or hydrochloric acid. It is insoluble in water, but soluble in alcohol, whence it crystallises in broad shining needles or laminæ. The alcoholic solution reddens litmus. The compound dissolves in caustic soda with purple, and in alkaline carbonates with blood-red colour. It gives by analysis 60·6 to 61·7 C, 4·2 to 4·3 H, and 11·2 to 11.0 Cl, which Schunck represents by the formula $C^{32}H^{12}ClO^{9}$, requiring 61·65 C, 3·85 H, 11·36 Cl, and 23·14 O. The formula $C^{16}H^{13}ClO^{5}$ requires 59·5 C, 4·0 H, and 11·1 Cl. An ammoniacal solution of chlororubiadin mixed wtth chloride of barium, filtered from the flocks which separate at first and left to itself in a closed vessel, deposits long red needles, which when dried at 100° contain 15·65 per cent. Ba″O, and may be represented by the formula $C^{32}H^{24}Ba''Cl^{2}O^{10}.2Ba''O$.

RUBIADIPIN. $C^{30}H^{24}O^{6}$? (Schunck, J. pr. Chem. lix. 474.)—A compound formed, together with many others, by the fermentation of madder.

Erythrozym is added to aqueous rubian, and the liquid is allowed to stand in a moderately warm place, until it has become tasteless and colourless, owing to the deposition of a brown jelly. If this deposit should not take place in 24 hours, more erythrozym must be added. Or madder is stirred up with cold or warm water, and left in a warm place till a jelly is formed. In both cases the mass is mixed with a little water, and the jelly is collected on a filter and washed with a small quantity of water. It contains alizarin, rubiretin, verantin, rubiafin, rubiagin, and rubiadipin, which are separated as follows:—

The mass is well boiled with alcohol as long as the liquid acquires a yellow colour, and acetate of aluminium is added to the filtrate, whereby alizarin, verantin, and rubiafin are precipitated in combination with alumina, but only partially. The whole is then filtered (for the further treatment of the precipitate, see below), and sulphuric acid and a large quantity of water are added to the dark brownish-red filtrate, whereby the whole of the dissolved substances are precipitated as a yellow powder, which, having been thoroughly washed with water, is redissolved in boiling alcohol, and mixed with excess of acetate of lead. The dark purple-red lead-precipitate, which is to be filtered boiling, contains alizarin, rubiretin, verantin, and rubiafin; the dark-yellow filtrate, rubiagin and rubiadipin.

On mixing this filtrate with a large quantity of water, a faintly orange-coloured precipitate is formed, consisting of the lead-compounds of rubiagin and rubiadipin; this precipitate is to be collected and decomposed by boiling dilute sulphuric acid. The undissolved portion washed with water, then boiled with alcohol, yields to the latter, rubiagin and rubiadipin, both of which remain, after evaporation of the alcohol, as a soft, dark-brown, fatty mass, and may be separated by cold alcohol, which dissolves chiefly the rubiadipin; the undissolved rubiagin may be purified by recrystallisation from hot alcohol.

Rubiadipin is a semifluid, yellowish-brown, fatty substance, which does not harden even when heated for a long time. In boiling water it melts to oily drops, which rise to the surface. It is insoluble in water, soluble in alcohol and in alkalis, forming with the latter a blood-red soapy liquid. The alcoholic solution forms, with neutral acetate of lead, a blood-red precipitate containing 31·35 per cent. lead-oxide, whence Schunck deduces the formula $C^{30}H^{24}O^{5}.PbO$.

RUBIAFIN. $C^{32}H^{13}O^{9}$? (Schunck, J. pr. Chem. lix. 465.)—A compound isomeric with rubiadin, produced, as already mentioned, in the fermentation of rubian. The lead-precipitate, containing alizarin, rubiretin, verantin, and rubiafin, obtained as described in the preceding article, is decomposed by boiling hydrochloric acid; and the precipitated yellow flakes are washed and covered with cold alcohol, which extracts rubiretin, leaving alizarin, rubiafin, and verantin. On the other hand, the above-mentioned precipitate produced by acetate of aluminium, is decomposed by boiling hydrochloric acid, whereby orange flakes are separated; and these are added to the residue of alizarin, rubiafin, and verantin, which was left undissolved by cold alcohol, and the whole is subjected to the following treatment:—The mixture is dissolved in boiling alcohol and mixed with acetate of copper, which forms a purple precipitate containing rubiafite and verantite, with a small quantity of alizarite of copper, while alizarin alone remains in solution. The purple copper-precipitate, decomposed by hydrochloric acid, deposits insoluble red flakes, which, after washing, are dissolved in boiling alcohol, and treated with hydrated stannous oxide; whereupon only *rubiafin* remains dissolved, and crystallises from the filtrate in brilliant needles and laminæ, while verantin, together with a small quantity of alizarin, is precipitated as a stannous oxide lake (Schunck). See VERANTIN.

Rubiafin forms yellow shining plates and needles, sometimes star- or fan-shaped masses, which behave like rubiacin when heated with water, sulphuric acid, nitric acid, neutral acetate of lead, and cupric acetate, and likewise form rubiacic acid when treated with ferric nitrate: in fact, rubiafin differs from rubiacin only in composition. It contains, according to Schunck, 69·3 per cent. carbon and 4·6 hydrogen (calc. 69·3 C, 4·7 H, and 26·0 O).

RUBIAGIN. (Schunck, J. pr. Chem. lix. 471.)—This is another of the compounds produced by the fermentation of rubian. For the mode of preparing it, see RUBIADIPIN (p. 120). It forms small yellow spherical granules, or concentrically grouped needles. It is insoluble in boiling water, dissolves in boiling alcohol more easily than rubiadin or rubianin, and with yellow colour in acetic acid, from which it crystallises on cooling. Alkalis, baryta-water, and lime-water dissolve it with blood-red colour. It dissolves in cold oil of vitriol, with dark brown-red colour, and in boiling nitric acid, forming a yellow liquid, which deposits shining crystals as it cools. When boiled with ferric chloride, it assumes a darker colour, but does not become purple-brown, like rubiafin and rubiacin. The alcoholic solution mixed with neutral acetate of lead turns yellow, and then throws down orange-coloured grains, which dissolve sparingly in boiling alcohol, easily in an alcoholic solution of neutral lead-acetate. This property distinguishes rubiagin from rubiacin, rubiadin, and rubiafin. With cupric acetate, the alcoholic solution of rubiagin forms an orange-coloured precipitate.

The composition of rubiagin is very uncertain, as it has not been obtained pure. Schunck found it to contain 68·10 per cent. C and 5·14 H. The formula $C^{16}H^{14}O^{5}$, which requires 67·12 C, 4·89 H, and 27·99 O, would explain its formation from rubian, as follows:—

$$\underset{\text{Rubian.}}{C^{28}H^{34}O^{15}} + 2H^2O = \underset{\text{Rubiagin.}}{C^{16}H^{14}O^5} + \underset{\text{Glucose.}}{2C^6H^{12}O^6}.$$

RUBIAN. $C^{28}H^{34}O^{15}$.—A glucoside existing in madder-root, and yielding, under the influence of acids, alkalis, or erythrozym (madder-ferment)—on the one hand, glucose, and on the other, alizarin, together with rubiretin, verantin, and other products, varying according to the nature of the decomposing compound. It was discovered by Schunck in 1847. (For references to his memoirs, see *Gmelin's Handbook*, xvi. 32.)

Preparation.—It is difficult to obtain this substance pure, inasmuch as it alters very quickly, and does not precipitate any metallic solution excepting basic acetate of lead, which when added to madder-extract, throws down othor substances at the same time. The best results are obtained by taking advantage of the great affinity of rubian for porous bodies, especially for animal charcoal.

One pound of Avignon-madder is exhausted on a cloth strainer, by pouring four or five quarts of boiling water upon it; the dark yellowish-brown, still hot filtrate is mixed with an ounce of bone-charcoal, stirred, and left to settle; the still brown liquid is decanted; and the residue is collected and washed with cold water, till the liquid which runs off becomes green when boiled with hydrochloric acid (from the presence of chlorogenin). The washed bone-charoal, if boiled with alcohol, as long as it colours the liquid yellow, yields to it the rubian which it has carried down; and on evaporating the alcoholic solution, the rubian is left behind, but still impure, containing chlorogenin. To remove the latter, the impure rubian, obtained in the manner just described, is again precipitated in the same manner on the previously used charcoal, which now takes up only the rubian, and again extracted by boiling alcohol, this series of operations being repeated a third time with the same bone-charcoal, in case the alcoholic solution still contains chlorogenin.* On evaporating the alcoholic solutions, the rubian remains behind, still retaining a small quantity of a decomposition-product formed by the action of heat. This is separated, either—*a.* By evaporating the greater part of the alcohol, mixing the solution when cold with dilute sulphuric acid (which throws down the decomposition-product in brown resinous drops), removing the sulphuric acid by carbonate of lead, then filtering, and evaporating over the water-bath; or—*b.* By precipitating the solution with neutral acetate of lead, filtering from the brown-red flocks which separate, and adding basic acetate of lead, whereby a compound of rubian with lead-oxide is precipitated, which must be washed with alcohol, and decomposed by sulphydric or dilute sulphuric acid. In the latter case, the excess of sulphuric acid must be removed, as in *a.*—One cwt. of madder yields 1,000 grammes of rubian.

The following process serves at the same time for the preparation of alizarin, rubiacin, rubiretin, and verantin:—Coarsely pulverised madder-root is well boiled with water (1lb. of the root to 16 quarts of water); the liquid, after several hours' boiling, is strained through calico (the residue, exhausted with water, still contains alizarin and rubiacin); and the liquid is precipitated with dilute sulphuric (or hydrochloric) acid. A dark-brown precipitate is thus obtained, which, when separated by decantation and filtration, and freed from excess of acid by washing with a quantity of cold water just sufficient for the purpose (a larger quantity dissolves rubiacin), contains seven substances, —viz. rubian, alizarin, rubiacin, rubiretin, verantin, pectic acid, and a dark-brown product of the decomposition of extractive matters. (The filtrate retains chlorogenin and a small quantity of sugar). The precipitate, while still moist, is boiled with alcohol, as long as the alcohol acquires a yellow colour, and the liquid is filtered hot. (In the residue there remains pectic acid and oxidised extractive matter). The dark-brown decoction, on cooling, frequently deposits *verantin* as a dark-brown resinous powder, which must be separated by filtration. The alcoholic solution, after being again heated to the boiling-point, is mixed and digested with recently precipitated hydrate of aluminium, till the solution is nearly decolorised, whereby alizarin, rubian, rubiacin, and part of the rubiretin and verantin are precipitated, while another portion of the two last-mentioned substances remains dissolved in alcohol.

a. Separation of Alizarin.—The alumina-precipitate, after being washed with alcohol, is added to a concentrated boiling solution of potassic carbonate; the deep red solution, containing all the other substances, is filtered from the undissolved compound of alizarin and alumina; this substance is repeatedly boiled with aqueous potassic carbonate, till the liquid, which runs off on filtration, exhibits only a faint purple colour; the residue is decomposed by boiling hydrochloric acid; and the alizarin thus separated is crystallised from alcohol.

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* As fresh bone-charcoal precipitates both rubian and chlorogenin, whereas charcoal, which has once been used for this purpose and boiled out with alcohol, precipitates only the former, or at least gives up only the former to boiling alcohol, it is best not to extract, for the purpose of purification, the first portion of rubian taken up by fresh bone-charcoal, but to use this charcoal for the preparation of purer rubian.

β. Of Rubian.—The deep red alkaline liquid, filtered from the compound of alizarin and alumina, still retains in solution, rubian, rubiacin, rubiretin, and verantin, which may all be precipitated by hydrochloric acid, then collected and washed with cold water, till the liquid which runs off is free from acid. As soon as this point is attained, the rubian, which is insoluble in acidulated water, begins to dissolve in the pure water, imparting to that which runs off a yellow colour and bitter taste; so that at length it is completely dissolved, and may be obtained as a yellow extract, by evaporating the filtrate. It still, however, retains pectic acid, which remains behind on dissolving the extract in alcohol, and from 5 to 8 per cent. ash, from which it cannot be separated.

γ. Of Rubiacin, Rubiretin, and Verantin.—The residue left after the rubian has been washed out, is mixed with that which remains on evaporating the alcoholic liquid above mentioned, containing verantin and rubiretin, and the mixture is treated with a boiling solution of ferric chloride or nitrate. Rubiretin and rubiacin then dissolve (the latter partly as such, partly converted, with assumption of oxygen, into ferric rubiacate, p. 119), while verantin remains behind in combination with ferric oxide. The deep red-brown solution is filtered after boiling for some time; the residue is kept for the preparation of verantin; the rubiacin, rubiacic acid, and rubiretin are thrown down from the filtrate as a yellow precipitate, turning brown during washing; and this precipitate, while still moist, is dissolved in boiling alcohol, which takes up the rubiacin and rubiretin, and deposits the former, on cooling, in small lemon-yellow crystals. (The rubiacic acid which remains in solution is purified in the manner already described, p. 119,—the crystallised rubiacin by converting it into rubiacic acid, from which it may be again obtained as rubiacin). By further evaporation of the alcohol, a mixture of rubiacin and rubiretin is obtained as a dark-brown-red residue, which, when boiled with water, deposits dark brown drops of rubiretin; whilst rubiacin remains suspended as a light powder, and may be removed by decantation. After boiling several times with water, as long as any yellow powder remains, and then decanting, rubiretin ultimately remains in the form of a dark red-brown mass.

Properties.—Rubian is a hard, dry, brittle, perfectly amorphous mass, resembling dried varnish or gum-arabic, not at all deliquescent, transparent, and deep yellow in thin layers, dark-brown in thicker masses. It is very soluble in *water*, somewhat less soluble in *alcohol*, and insoluble in *ether*, which precipitates it from the alcoholic solution in brown drops. The solutions are very bitter.

Rubian dried at 100° (after deduction of 5·30—7·69 per cent. ash, consisting chiefly of calcic carbonate), contains, according to Schunck, 54·85 per cent. carbon, 5·57 hydrogen, and 39·58 oxygen, whence he deduces the formula $C^{28}H^{34}O^{15}$, requiring 55·08 C, 5·57 H, and 39·35 O. This formula serves to account for the several transformations of rubian observed by Schunck, supposing that the formulæ assigned to the several products, alizarin, rubiretin, rubiadin, &c., are correct. This, however, is very doubtful, especially with regard to the most important and best-defined of these products, viz. alizarin, to which Schunck assigns the formula $C^{14}H^{10}O^{4}$, representing its formation from rubian by the equation:

$$C^{28}H^{34}O^{15} = 2C^{14}H^{10}O^{4} + 7H^{2}O.$$

Other chemists, however, represent alizarin by the formula $C^{10}H^{6}O^{3}$, which agrees nearly as well with the results of analysis, and gives a clearer view of the other chemical relations of alizarin, especially to phthalic acid (i. 114). Hence Gerhardt (*Traité*, iii. 492) suggested for rubian (dried at 100°) the formula $C^{16}H^{16}O^{8}.\frac{1}{2}H^{2}O$, (requiring 55·87 C, 4·94 H, and 39·25 O), according to which the formation of alizarin is represented by the equation:

$$\underset{\text{Rubian.}}{C^{16}H^{16}O^{8}} + H^{2}O = \underset{\text{Alizarin.}}{C^{10}H^{6}O^{3}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}}$$

It is not very easy to explain the formation of the other derivatives of rubian by Gerhardt's formula, especially that of rubianic acid; but, as already observed, the formulæ assigned by Schunck to these compounds are very doubtful, many of them being founded on analyses evidently made upon impure preparations. The whole subject therefore requires further investigation.

Decompositions.—1. Rubian heated in a test-tube decomposes, and gives off water at 130°; at a higher temperature, it emits orange-coloured vapours, chiefly consisting of alizarin, and leaves much charcoal.

2. Heated on platinum-foil, it melts, swells up, burns with flame, and leaves a mixture of charcoal and ash.

3. Aqueous rubian, evaporated by heat in contact with the *air*, deposits dark-brown

resinous drops, the quantity of which increases on pouring water upon the residue, and again evaporating. The drops of resin melt in boiling water, become brittle on cooling, yield, when heated in a test-tube, a copious, yellow, transparent sublimate, resembling rubiacin, and behaving in a similar manner to ferric chloride; they are probably, therefore, a mixture of rubiretin and rubiacin.

4. *Chlorine* passed into aqueous rubian throws down yellow flocks of chlororubian, while glucose remains in solution:

$$\underset{\text{Rubian.}}{C^{28}H^{34}O^{15}} + 3H^2O + Cl^2 = \underset{\text{Hydrochlorate of chlororubian.}}{C^{22}H^{27}ClO^{12}.HCl} + C^6H^{12}O^6.$$

The continued action of the chlorine ultimately produces perchlororubian. *Chloride of lime* converts rubian into phthalate of calcium.

5. Aqueous rubian is not altered by cold *nitric acid*, but at the boiling heat red fumes are evolved; and the rubian is completely converted into phthalic acid, without formation of oxalic acid or any insoluble residue.

6. *Oil of vitriol* dissolves rubian, with blood-red colour, and blackens it on boiling, with evolution of sulphurous acid.

7. When aqueous rubian is boiled with dilute *sulphuric* or *hydrochloric acid*, the solution first becomes opalescent, and then deposits orange-coloured flocks, containing alizarin, rubiretin, verantin, and rubianin, while sugar remains in solution. [For the equations representing the formation of these products, see MADDER, iii. 746.]

8. In contact with aqueous *alkalis*, *alkaline earths*, or the *acid carbonates of the alkaline earth-metals*, and *air*, rubian takes up oxygen, and is converted into rubianic acid, rubidehydran, and rubihydran,—small quantities of acetic acid, rubiadin, and sugar being formed at the same time.

a. Formation of rubianic acid:

$$\underset{\text{Rubian.}}{C^{28}H^{34}O^{15}} + O^5 = \underset{\text{Rubianic acid.}}{C^{26}H^{30}O^{14}} + 2CO^2 + 2H^2O$$

or

$$\underset{\text{Rubian.}}{C^{28}H^{34}O^{15}} + O = \underset{\text{Rubianic acid.}}{C^{26}H^{30}O^{14}} + \underset{\text{Acetic acid.}}{C^2H^4O^2}.$$

β. Of rubidehydran:

$$C^{28}H^{34}O^{15} = C^{28}H^{32}O^{14} + H^2O.$$

γ. Of rubihydran:

$$C^{28}H^{34}O^{15} + 3H^2O = C^{28}H^{40}O^{18}.$$

9. Rubian boiled with excess of *caustic potash*, or *soda*, dissolves with blood-red colour, changing to purple-red; and by continued boiling is completely resolved into alizarin, rubiretin, verantin, and rubiadin, which are precipitable by acids, and sugar, which remains in solution. The same products are formed, though more slowly, by boiling with caustic *baryta*. [MADDER, iii. 746.]

Ammonia colours aqueous rubian blood-red, but does not decompose it, even at t boiling heat.

Magnesia colours aqueous rubian blood-red; the carbonates of calcium and barium do not act upon it; aluminic, ferric, and cupric hydrates extract all the rubian from it.

The alkaline solutions of rubian reduce *gold-salts*, but not silver or copper-salts.

10. *Erythrozym*, added to an aqueous solution of rubian, diffuses itself through the liquid without dissolving, rendering it turbid and gummy, and converting it, after standing for some time in a moderately warm place, into a brown jelly, like coagulated blood, containing yellow striæ and flocks formed of long capillary crystals, till finally (more erythrozym being added if necessary) the liquid becomes tasteless and colourless, and a gelatinous mass separates, consisting of alizarin, verantin, rubiretin, rubiafin, rubiagin, and rubiadipin (iii. 746; v. 120). The solution retains sugar and pectic acid. During the fermentation, the liquid remains neutral, neither absorbing nor giving off gases: access of air is likewise unnecessary.

Derivatives of Rubian.

Chlororubian, $C^{22}H^{27}ClO^{12}$. (Schunck, Phil. Mag. [4] xii. 200, 270.)—A compound formed, together with glucose, by the action of chlorine on aqueous rubian. To prepare it, an aqueous extract of madder is precipitated with neutral acetate of lead, the filtrate precipitated with ammonia, the resulting red precipitate decomposed by sulphuric acid, and chlorine gas passed into the filtrate. The dirty yellow flocks of an easily fusible resin, which are precipitated by the first action of the chlorine, are separated by filtration; and the pure yellow flocks of chlororubian, precipitated on continuing the passage of the chlorine, are collected and crystallised from hot alcohol.

When crystallised from dilute alcoholic solution, it forms light orange-yellow needles, having a bitter taste; precipitated from concentrated alcoholic or hot aqueous solution, it forms granular amorphous spherules. It is neutral; dissolves with yellow colour in boiling water, also in alcohol; does not dye mordanted tissues. It gives by analysis 51·18 per cent. C, 4·93 H, and 6·38 Cl, the formula requiring 50·92 C, 6·82 H, 5·20 Cl, and 37·51 O.

Chlorine-water gradually converts chlororubian into perchlororubian. By boiling dilute *sulphuric* or *hydrochloric acid*, it is resolved into chlororubiadin (p. 120) and glucose:

$$C^{22}H^{27}ClO^{12} = C^{16}H^{11}ClO^{4} + C^{6}H^{12}O^{6} + 2H^{2}O.$$

With caustic *soda* it forms a blood-red solution, which after being heated for some time deposits dark red-brown flocks of oxyrubian, while sugar and its products of decomposition, together with verantin, rubiretin, and rubiadin, remain in solution.

Oxyrubian, after boiling with hydrochloric acid, washing with boiling alcohol, and drying, is a yellowish-brown powder, which if free from chlorine, yields, when heated in a test-tube, a yellow crystalline sublimate, easily soluble in alkalis. It is not altered by sulphide of ammonium, but alkalis turn it red-brown. It contains, according to Schunck, 70·7 C, 3·9 H, and 25·4 O, which may be represented by the formula $C^{22}H^{14}O^{6}$; its formation may take place according to the equation:

$$C^{22}H^{27}ClO^{12} + NaHO = C^{22}H^{14}O^{6} + NaCl + 7H^{2}O.$$

Perchlororubian, $C^{44}H^{18}Cl^{18}O^{18}$. (Schunck, *loc. cit.*)—This compound, recrystallised from boiling alcohol, forms colourless transparent four-sided plates, having a splendid iridescence. It is neutral, sublimes in micaceous scales when cautiously heated, is insoluble in water, soluble in alcohol and ether; gives by analysis 37·05 C, 1·51 H, 44·40 Cl, the formula requiring 37·09 C, 1·26 H, 44·47 Cl, and 16·88 O.

RUBIANIC ACID. $C^{26}H^{30}O^{14}$? (Schunck, Phil. Mag. [4] xii. 200, 270.)—An acid, produced, together with rubihydran and rubidehydran, by the oxidation of rubian in contact with alkalis (iii. 746).

Preparation: 1. *From Rubian.*—Carbonic acid gas is passed into a solution of rubian mixed with excess of baryta-water, till the baryta is converted into acid carbonate, and the filtrate is left to stand in contact with the air. The liquid, after some time, becomes covered with thin scarlet films, presenting a crystalline appearance under the microscope (compounds of baryta with rubianic acid and rubidehydran), more of which are obtained after longer standing, and again on evaporating the liquid, finally in the form of red flocks, whilst rubihydran remains dissolved in the brownish-yellow liquid (sometimes also sugar resulting from a secondary decomposition). The collected films and flocks are decomposed with dilute sulphuric acid; the excess of that acid is precipitated by carbonate of lead; the precipitate is repeatedly boiled with water, till it exhibits only a faint reddish tint (in which state it contains no impurity except a small quantity of rubiadin, produced by secondary decomposition), and the solution is filtered and evaporated; a yellow-brown mass then remains, mixed with yellow needles, from which cold water extracts rubidehydran, leaving rubianic acid in the form of a yellow powder. This product is washed with cold water, and recrystallised from boiling water, if necessary with aid of animal charcoal.

2. *From Madder, without previous preparation of Rubian.*—Extract of madder prepared with hot water is precipitated with neutral acetate of lead, then the filtrate with basic acetate; and the latter precipitate, containing rubian and chlorogenin, is decomposed by cold dilute sulphuric acid, digested with carbonate of lead, and filtered. The filtrate, treated with baryta-water, then with carbonic acid, as in the first method, deposits, after standing for some time in contact with the air, rubianate of barium and the barium-compound of rubidehydran, to be treated as in 1, while rubidehydran and chlorogenin remain in solution.

Properties.—Rubianic acid forms lemon-yellow silky needles; in the impure state, granules and a crystalline mass. Tastes somewhat bitter. Reddens litmus.

It gives by analysis 55·5 to 56·6 per cent. C, and 5·4 to 5·6 H, whence Schunck deduces the formula $C^{52}H^{56}O^{27}$ (calc. 56·0 C, 5·2 H, 38·8 O). The formula $C^{26}H^{30}O^{14}$ requires 55·1 C, 5·3 H, and 39·6 O.

Rubianic acid dissolves more easily in boiling than in cold water; also in alcohol, but not in ether; does not dye mordanted fabrics. It dissolves without decomposition in hot aqueous *phosphoric*, *acetic*, *oxalic*, and *tartaric acids*. Its salts are red; those of the *alkali-metals* are easily soluble; the rest are formed by precipitation.

Rubianic acid when strongly heated yields a sublimate of alizarin, and a residue of charcoal; by boiling with dilute sulphuric acid it is resolved into alizarin and glucose:

$$C^{26}H^{30}O^{14} + 2H^{2}O = C^{14}H^{10}O^{4} + 2C^{6}H^{12}O^{6}.$$

RUBIANIN. A body obtained, together with alizarin, rubiretin, and verantin, by boiling aqueous rubian (or the extract of madder prepared with boiling water) with dilute sulphuric acid. The orange-yellow flocks thereby deposited, which contain the four substances, are dissolved in boiling alcohol, the reddish-yellow solution is filtered boiling, and the residue is boiled with fresh alcohol as long as the latter acquires a dark-yellow colour. The yellow or brownish-yellow crystalline mass left in the residue is chiefly rubianin, which, however, may also be dissolved by frequent treatment with boiling alcohol, whence it crystallises on cooling, as well as from the first extracts. The solutions are left to cool, and the crystals of rubianin containing verantin are separated from the mother-liquid (which, however, still contains a little rubianin), and dissolved in boiling alcohol; the verantin is precipitated by acetate of lead, and the filtrate is left to cool, whereupon it deposits crystals of rubianin. (See further *Gmelin's Handbook*, xiv. 133, 134.)

Rubianin crystallises in lemon-yellow needles having a silky lustre, and lighter in colour than rubiacin. It contains (at 100°) 57·6 per cent. C and 5·42 H, whence Schunck deduces the formula $C^{32}H^{38}O^{15}$ (requiring 58·0 C, 5·7 H. and 36·3 O. Gerhardt (*Traité*, iii. 493) suggested the formula $C^{10}H^{10}O^{5} = C^{10}H^{6}O^{3}$ (alizarin) + $2H^{2}O$ (calc. 57·1 C, 4·8 H).

Rubianin is more soluble in boiling water than rubiacin, less soluble in alcohol than rubiretin or verantin. Chlorine converts it into perchlororubian (?). It dissolves with yellow colour in cold oil of vitriol, and without decomposition in hot, strong, nitric acid. It is insoluble in the cold in ammonia, carbonate of potassium, and carbonate of sodium, but dissolves at the boiling heat, forming a blood-red solution, whence it crystallises after standing for some time.—The ammoniacal solution forms red precipitates with chloride of barium and chloride of calcium. The alcoholic solution does not precipitate neutral acetate of lead. Rubianin dissolves with dark-brown colour in a strong solution of ferric chloride, without forming rubiacic acid.

RUBICHLORIC ACID. (Rochleder, Ann. Ch. Pharm. lxxx. 327; R. Schwarz, *ibid.* lxxx. 333; Willigk. *ibid.* lxxxii. 339.)—This acid, perhaps identical with Schunck's chlorogenin (i. 921), is contained, according to Rochleder, in the root, according to Willigk, in the leaves, of *Rubia tinctorum*; also, according to Schwarz, in the herb of *Asperula odorata*, *Galium verum*, and *G. aparine*. It is found in traces in the precipitate formed by neutral acetate of lead in the aqueous extracts of the plants just mentioned; in somewhat larger quantity in the precipitate produced in the filtrate by basic acetate of lead; and chiefly in the precipitate thrown down by ammonia in the liquid filtered from the preceding precipitates, and still containing lead. It is separated therefrom by sulphydric acid. (For the details of the preparation, see *Gmelin's Handbook*, xvi. 67.)

Rubichloric acid is a colourless or slightly yellow mass, having no odour, but a faint nauseous taste; easily soluble in water and alcohol, insoluble in ether, coloured yellow by alkalis, not precipitated by baryta-water. Its *lead-salt*, obtained by precipitating the ammoniacal solution with neutral acetate of lead, is a yellow transparent mass. The results obtained by its analysis are so discordant that it is useless to quote them. The acid itself has not been analysed.

Rubichloric acid heated with hydrochloric acid turns blue, then green, and deposits dark-green flocks of chlororubin, with simultaneous production of formic acid; perhaps thus:—

$$\underset{\text{Rubichloric acid.}}{C^{14}H^{16}O^{9}} = \underset{\text{Chlororubin.}}{C^{12}H^{8}O^{3}} + \underset{\text{Formic acid.}}{2CH^{2}O^{2}} + 2H^{2}O.$$

Chlororubin.—This body is likewise produced by boiling chlorogenin with acids (Schunck). According to Jessen (Wien. Akad. Ber. xiv. 294), it is contained in Chinese yellow pods, the fruit of *Gardenia grandiflora*, and may be prepared therefrom by distilling the alcoholic decoction in a stream of carbonic anhydride, to remove the alcohol, passing the liquid through a wet filter to free it from oil, and treating the filtrate with neutral acetate of lead, which throws down colouring matters and tannic acid. On gently warming the filtrate with hydrochloric acid and heating it to the boiling-point, after removing the brown flocks which separate at first, chlororubin is deposited in dark-green flocks, which may be washed with water and dried in a vacuum. It then forms a blue-green, grass-green, or black-green powder, containing variable quantities of water. It is insoluble in water and in alcohol, but dissolves in alkalis, forming a blood-red solution, which is turned green by acids. It gives by analysis: (*a*) 63·8 per cent. C, 5·0 H (Debus); (*b*) 68·6 C, 4·4 H (Rochleder); (*c*) 61·17 C, 5·1 H (Schwarz).

According to Rochleder, anhydrous chlororubin contains $C^{12}H^{8}O^{3}$, and it is associated in *a* with $\frac{3}{2}$ at., in *b* with $\frac{1}{2}$ at., and in *c* with 2 at. water. According to v. Orth

(Wien. Akad. Ber. xiii. 510), it contains, after deduction of 5·9 per cent. ash, 74·8 C and 6·46 H, whence he deduces the formula $C^{48}H^{50}O^{9}$.

RUBIDEHYDRAN. $C^{28}H^{32}O^{14}$. (Schunck, Phil. Mag. [4] xii. 200.)—Obtained in aqueous solution in the preparation of rubianic acid, and partly purified by evaporation, solution in cold water, and precipitation with alcohol. It forms a reddish-yellow, transparent, non-deliquescent, bitter gum, yielding with water a yellowish solution, from which it is not precipitated by any metallic salt, except basic acetate of lead. It gave by analysis 56·50 C and 5·65 H; the above formula, which is that of rubian *minus* 1 at. water, requires 56·75 C, 5·40 H, and 38·87 O.

RUBIDINE. $C^{11}H^{17}N$. (G. Thenius, Rép. Chim. app. iv. 181; Jahresb. 1861, p. 500.)—An organic base belonging to the pyridine series, $C^{n}H^{2n-5}N$, and contained, together with several other members of that series, in coal-tar. The method adopted by Thenius for obtaining these bases from coal-tar oil, and separating them one from the other, is similar to that given by Greville Williams under PICOLINE (iv. 636); consisting in combining the bases with sulphuric acid, liberating them by caustic soda, dehydrating them with caustic potash, and separating them by fractional distillation, or by fractional precipitation as platinum-salts.

Rubidine, so called from the tendency of most of its salts to assume a reddish tint on exposure to the air, is a colourless liquid, having a faint odour and oily consistence. It is heavier than water (specific gravity = 1·017), slightly soluble therein, soluble in all proportions in alcohol, ether, and volatile oils. At 17° it thickens, but does not solidify. Boils at 230°.—With *chloride of lime* it produces a red colour, which does not entirely disappear on addition of acids. Fir-wood moistened with hydrochloric acid is also coloured red by it. The base precipitates alumina, chromic oxide, and ferric oxide from solutions of their salts, but not lime, baryta, or magnesia.

The solutions of rubidine in acids leave, when evaporated over the water-bath, gummy masses, which solidify in the crystalline form on standing over chloride of calcium. The *hydrochlorate* forms, with *mercuric chloride*, a double-salt which melts at 32°, and crystallises from hot water in needles, turning somewhat reddish in contact with the air. The *platinum-salt*, $2C^{22}H^{18}NCl.Pt^{iv}Cl^{4}$, is a reddish crystalline powder, insoluble in water, alcohol, and ether. With *chloride of gold*, the solution of the base in hydrochloric acid forms a yellowish-red, sparingly soluble double salt.

RUBIDIUM. *Symbol*, Rb.; *Atomic Weight*, 85·4.—A metal, belonging to the group of elements which likewise includes lithium, sodium, potassium, and cæsium. It was discovered by Kirchhoff and Bunsen in 1860, by the method of spectral analysis. Its spectrum is chiefly distinguished by two bright red lines, situated beyond the line A: hence the name of the metal (*ρυβιδος*, dark-red).

Rubidium was first detected, together with cæsium, in the mineral water of Dürckheim, in which it exists to the amount of 2 pts. in ten million. It has since been found in larger quantity, together with cæsium and lithium, in several other saline waters (see CÆSIUM, i. 1113), and most abundantly in that of Bourbonne-les-Bains, a litre of which contains 0·034 grm. chloride of potassium, 0·032 grm. chloride of cæsium, and 0·019 grm. chloride of rubidium (Grandeau, Ann. Ch. Phys. [3] lxvii. 155); and in that of Nauheim, the mother-liquor of which yields a residue containing in a pound, 2 drachms 9 grains of the chlorides of rubidium and cæsium. (Böttger, Ann. Ch. Pharm. cxxvii. 368; cxxviii. 240.)

Rubidium is also found in several lepidolites; that of Rozena, in Moravia, contains 0·24 per cent. rubidium, with only a trace of cæsium; that of Hebron, in the State of Maine, 0·24 per cent. rubidium and 0·3 per cent. cæsium. The two metals likewise occur, though in smaller quantity, in the lepidolite of Prague, the petalite of Utö in Finland, the lithia-mica of Zinnwald in Bohemia, triphylline, and other lithia minerals. The melaphyre of Norheim, in which the mineral waters of Dürckheim and Kreuznach take their rise, contains, according to Laspeyres (Bull. Soc. Chim. 1866, i. 356) 0·00038 per cent. oxide of cæsium, and 0·000298 per cent. oxide of rubidium.

Lastly, rubidium has been found in the ashes of many plants, and in the salin or crude potash obtained from the residue of the beetroot sugar manufacture (iv. 713). According to Grandeau, the salin of the North of France contains 1·8 grm. rubidium-chloride in a kilogramme. The quantity of this salt annually abstracted from the soil amounts to about 260 grms. per hectare, although the proportion of rubidium existing in the soil is too small to be detected, even by spectral analysis. Rubidium has also been found in tobacco-leaves, in coffee, tea, cocoa, and crude tartar. In minerals and mineral-waters, rubidium and cæsium are always associated with lithium, and generally also with potassium and sodium; but plants have the power of assimilating two or three of these metals, to the exclusion of the rest: thus tea, coffee, and the salin of beetroot contain potassium, sodium, and rubidium, but not a trace of lithium.

Preparation.—The best source of rubidium, according to Bunsen, is the saline residue obtained in the preparation of lithia from Saxon lepidolites, and consisting of the chlorides of sodium, potassium, and rubidium, with small quantities of chloride of cæsium, and traces of chloride of strontium. The rubidium is precipitated, together with potassium and cæsium, by platinic chloride, and separated from potassium by the inferior solubility of its chloroplatinate (i. 1114). One kilogramme of the saline mixture is dissolved in 2·5 kilogrms. of water, and the cold liquid is precipitated by a solution of about 30 grms. platinum in nitromuriatic acid. After the precipitate has completely settled down, the supernatant liquid is decanted, and the precipitate is boiled 25 times in succession with small quantities of water (about 1·5 kilogrm. in all), each portion being then poured into the original liquid decanted from the precipitate. A fresh precipitation of platinum-salt is thereby produced, and the liquid decanted therefrom is to be evaporated down to nearly its original bulk (2·5 kilogrammes). If now the precipitated chloroplatinate be decomposed by hydrogen, and the reduced platinum washed, redissolved in nitromuriatic acid, and added to the liquid, a new precipitate will be formed, related to the solution in the same manner as at the beginning of the process. The precipitate and liquid may therefore be again treated as before.

By repeating this operation seven or eight times, the greater part of the rubidium-chloride contained in a kilogramme of the same material will be extracted. Each of the precipitates thus obtained is dried over the water-bath, the whole reduced by hydrogen, and the alkaline chlorides dissolved out by water. The product thus obtained consists of 125 grms. chloride of rubidium, mixed with 3 or 4 per cent. chloride of potassium, and a very small quantity of chloride of cæsium. To remove these impurities, the boiling solutions of 36 grms. of the mixed chlorides, and of the platinic chloride produced by dissolving 30 grms. platinum in nitromuriatic acid, are mixed together, and the yellow sandy precipitate, which separates on cooling to 40°, is washed by decantation with water at 40°—50°. The washed precipitate is reduced by hydrogen at as low and regular a temperature as possible, and the same treatment is repeated till the precipitate, when examined by the spectroscope, no longer exhibits the red ray peculiar to potassium (Bunsen, Ann. Ch. Pharm. cxxii. 351). The chloride of rubidium thus purified no longer contains any foreign metal except cæsium, from which it may be separated by the processes already described (i. 1113, 1114).

The same process may of course be applied to other mother-liquors and residues containing cæsium and rubidium. Böttger (*loc. cit.*) recommends the saline residue obtained by evaporating the mother-liquor of the Nauheim water as the cheapest and most productive source of these metals.

A modification of the preceding process is given by Heintz. (J. pr. Chem. lxxxvii. 310; Jahresb. 1862, p. 121; further, Ann. Ch. Pharm. cxxxiv. 129; Bull. Soc. Chim. 1865, ii. 354.)

The following process, applicable on the large scale, for extracting the alkali-metals from lepidolite is given by Schrötter (Wien. Akad. Ber. i. [2] 268; Bull. Soc. Chim. 1865, ii. 106; Jahresb. 1864, p. 186):—The mineral is first heated to redness, without the addition of any flux. It then melts with considerable tumefaction, and when subsequently thrown into cold water, solidifies to a vitreous transparent mass, which must be pulverised and washed. (The wash-waters contain small quantities of the alkali-metals, and may be used for the treatment of another portion of the mineral). The washed mass is boiled with hydrochloric acid (2 pts. of acid of specific gravity 1·10 to 1 pt. of lepidolite) for several hours, whereby the greater part of the silica is separated; and the solution, after addition of ferric nitrate, is mixed with carbonate of sodium, which precipitates iron, aluminium, calcium, magnesium, and manganese, the liquid being sufficiently diluted to prevent the simultaneous precipitation of carbonate of lithium. The filtered liquid deposits on evaporation a small additional quantity of magnesium-carbonate, and then retains nothing but the alkaline chlorides and a small quantity of silica. It is saturated with hydrochloric acid, and mixed with an aqueous solution of potassic chloroplatinate in sufficient quantity (determined by previous trial) to precipitate the whole of the rubidium, cæsium, and thallium. The filtered liquid, containing the excess of platinum and lithium, is precipitated by sulphydric acid to separate the platinum; then concentrated, and treated with carbonate of sodium, which throws down the lithium as carbonate.

The platinum-precipitate containing rubidium, cæsium, and thallium, is reduced by hydrogen at as low a temperature as possible; the ignited mass is washed with water, to remove the chlorides of cæsium and rubidium; then treated with sulphuric acid, and again washed with water, to dissolve out the thallium-salt. Lastly, the cæsium and rubidium are separated by the processes already mentioned.

This process, according to Schrötter, may be applied to all minerals containing lithium: 1000 pts. of lepidolite thus treated yield 78 pts. carbonate of lithium, 6·5 pts. chlorides of cæsium and rubidium, and 0·6 pt. thallium—supposing the preparation to be continuously carried on. (For remarks on Schrötter's process, see v. Hauer, Bull. Soc. Chim. 1865, ii. 352.)

According to Redtenbacher (Bull. Soc. Chim. 1865, ii. 201), potassium, cæsium, and rubidium may be separated by the different solubilities of their alums at 17°, 100 pts. of water at that temperature dissolving 13·5 pts. of potassium-alum, but only 2·27 pts. of rubidium-alum, and 0·619 pt. of cæsium-alum.

Metallic Rubidium was first obtained by electrolysis of the fused chloride, the positive pole being formed of graphite, the negative pole of an iron wire; but the metal, as fast as it was isolated, rose to the surface of the fused mass, and burnt with a reddish flame. By using, instead of pure rubidium-chloride, a mixture of the chlorides of rubidium and calcium in equivalent qantities, and heating it to a temperature a little below redness, a fused mass is obtained at the negative pole, which, when thrown into water, causes a brisk evolution of hydrogen—the gas carrying with it small globules of metal, which burn on the surface of the water. This method, however, does not yield the metal in sufficient quantity to allow of an examination of its properties. On the other hand, an amalgam of rubidium is easily formed by electrolysing a strong neutral aqueous solution of rubidium-chloride, using mercury as the negative and a platinum-wire as the positive pole of the battery. The mercury then takes up the rubidium, becoming heated at the same time, and the resulting amalgam forms on cooling a brittle, crystalline, silver-white mass. It decomposes water at common temperatures, and oxidises in the air, becoming covered with a crust of rubidic hydrate.

Rubidium is obtained in larger quantity by heating a mixture of 89·55 pts. acid tartrate of rubidium, 8·46 neutral tartrate of calcium, and 1·99 soot from oil of turpentine, in a furnace similar to that used for the reduction of potassium (iv. 693), and collecting the volatilised metal in a receiver containing mineral naphtha: 75 grms. of the acid tartrate thus treated yield 5 grms. of rubidium.

Properties.—Rubidium is a white metal, with a tinge of yellow, and a silvery lustre. Specific gravity = 1·52. It is as soft as wax, even at −10°, melts at 38·5°, and is converted, even below a red heat, into a greenish-blue vapour. When exposed to the air, it instantly becomes covered with a blue-grey film of suboxide, and takes fire in a few minutes even more easily than potassium. It is decidedly more electropositive than potassium, when formed into a circuit with the latter in acidulated water. When thrown on water it takes fire, with violent evolution of hydrogen, and burns with a flame exactly like that of potassium. It burns with vivid incandescence in the vapour of chlorine, bromine, iodine, sulphur, and arsenic, and acts as a reducing agent in the same manner as potassium. (Bunsen, Ann. Ch. Pharm. cxxv. 367; Jahresb. 1863, p. 185.)

RUBIDIUM, BROMIDE OF. RbBr.—Prepared by dissolving the carbonate in hydrobromic acid; crystallises in permanent shining cubes with subordinate octahedral faces and cubic cleavage; soluble in 104·8 pts. water at 16°, and in 5·98 pts. at 100°. (Reissig, Ann. Ch. Pharm. cxxvii. 33; Jahresb. 1863, p. 186.)

RUBIDIUM, CHLORIDE OF. RbCl.—The hot solution of the hydrate or carbonate in hydrochloric acid yields, by cooling or rapid evaporation, confused crystals; by slow evaporation, cubic crystals having a vitreous lustre and easily cleavable. They are anhydrous, permanent in the air, decrepitate when heated. The chloride melts at an incipient red heat, and volatilises perfectly in the blowpipe flame on platinum-wire. 100 pts. of water dissolve 76·38 pts. rubidium-chloride at 1°, and 82·89 pts. at 7°. (Bunsen, Jahresb. 1861, p. 176.)

Chloroplatinate of Rubidium, $2RbCl.Pt^{iv}Cl^4$, is obtained by precipitation as a light-yellow, sandy, anhydrous powder, consisting of microscopic regular octahedrons, insoluble in alcohol, and much less soluble in water than chloroplatinate of potassium. (See Table of Solubilities given under CÆSIUM, i. 1114.)

RUBIDIUM, CYANIDE OF. Small cubic crystals, which decompose very easily (Reissig).—The *ferrocyanide*, $Rb^4Fe''Cy^6.2H^2O$, is obtained by boiling ferrocyanide of iron free from potash (prepared by precipitating ferrous acetate with prussic acid, and exposing the washed precipitate to the air), with hydrate of rubidium, filtering, neutralising with acetic acid, and precipitating with alcohol. The light-yellow crystals, deposited from a hot solution on cooling, appear to be triclinic. (Piccard, Rép. Chim. pure, v. 254: Jahresb. 1862, p. 125.)

RUBIDIUM, DETECTION AND ESTIMATION OF. The compounds of rubidium so closely resemble the corresponding compounds of potassium and cæsium, that they cannot be distinguished therefrom by ordinary analytical methods; but by spectral analysis, very minute quantities may be detected. The spectrum of rubidium is continuous in the middle part, like that of potassium, but somewhat less bright; it is especially characterised by two strong red lines, Rbα and Rbβ, situated beyond Fraunhofer's line A, and the two others, γ and δ, less distinct, and likewise situated beyond A. These lines are most distinctly seen with the nitrate, chlorate, perchlorate, and chloride of rubidium, on account of the facility with which these salts are decomposed by heat. A drop of water weighing 4 milligrammes, and holding in solution only 0·002 milligrm. of the chloride, shows the lines α and β very distinctly. The sulphate also gives a fine spectrum, and even with the silicate and phosphate, all parts of the spectrum may be distinctly seen. (Bunsen and Kirchhoff.)

Estimation and Separation.—In a solution not containing potassium or cæsium, rubidium may be estimated in the same manner as potassium. The separation of rubidium from potassium is effected, as already described, by the inferior solubility of its chloroplatinate (p. 128). Heintz (J. pr. Chem. lxxxvii. 320; Jahresb. 1862, p. 121) has observed, that when a mixture of the chlorides of sodium, potassium, and rubidium is treated with a quantity of platinic chloride more than sufficient to convert all the rubidium into chloroplatinates, and then boiled down to a small bulk, the supernatant liquid retains only a trace of rubidium. If, on the contrary, the platinic chloride be added in quantity less than sufficient to precipitate the whole of the rubidium, and the liquid be kept for some time at a suitable temperature, the precipitate will consist wholly of chloroplatinate of rubidium.

For quantitative estimation, however, it is best to resort to indirect methods. Bunsen (Ann. Ch. Pharm. cxxii. 347) gives the following:—

α. The two metals are precipitated together by platinic chloride, and the amount of platinum in the precipitate is determined by the loss of weight consequent on reduction by hydrogen, and subsequent washing. Let A be the weight of the precipitate, B the loss of weight caused by reduction, &c., x the weight of the potassic chloroplatinate ($KPtCl^3$)* in the precipitate, y that of the corresponding rubidium-salt; then

$$x + y = A,$$

$$\frac{2Cl}{Pt + K + 3Cl}x + \frac{2Cl}{Pt + Rb + 3Cl}y = B;$$

whence x and y may be calculated.

As, however, commercial platinum often contains impurities, which may render its atomic weight incorrect by several hundredths, it is more exact: β. To weigh the mixture of the chlorides of potassium and rubidium obtained by washing the reduced precipitate, and determine the quantity of chlorine contained therein by precipitation with nitrate of silver.

Let x be the weight of potassium-chloride, y that of rubidium-chloride, A the weight of the mixture found by experiment, B that of the precipitated chloride of silver: then

$$x + y = A;$$

$$\frac{Ag + Cl}{K + Cl}x + \frac{Ag + Cl}{Rb + Cl}y = B.$$

$$\text{whence, if } \frac{Ag + Cl}{K + Cl} = a; \quad \frac{Ag + Cl}{Rb + Cl}y = b,$$

we find:

$$x = \frac{bA - B}{b - a}; \qquad y = A - x.$$

Atomic Weight of Rubidium.—Determined in the same manner as that of potassium. According to the mean of Bunsen's experiments, it is 85·36; according to Piccard, 85·41: hence 85·4 may be regarded as correct.

RUBIDIUM, FERROCYANIDE OF. (See page 129.)

RUBIDIUM, HYDRATE OF. $RbHO$, or $Rb^2O.H^2O$. Obtained by gradually adding baryta-water to a solution of the sulphate in 100 pts. water deprived of air by boiling. If the liquid be kept near the boiling point at the time of adding the baryta-water, and agitated, the precipitated barium-sulphate settles down in a few minutes, and the filtrate evaporated in a silver retort, yields hydrate of rubidium in the form of a white porous mass, with slightly greyish reflex. It melts at a heat below redness, without loss of water, and forms on cooling a brittle, slightly friable, amorphous mass, having a lamellar fracture. It volatilises completely in the blowpipe flame, dissolves in water with great rise of temperature, deliquesces rapidly on exposure to the air, forming a syrupy liquid, which is greasy to the touch, corrodes the skin, and, on continued exposure to the air, is gradually transformed into acid carbonate of rubidium, In short, hydrate of rubidium possesses alkaline and caustic properties as powerful as those of hydrate of potassium. It dissolves in alcohol, like caustic potash. It cannot be fused in platinum-vessels because it attacks them.

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* $Pt = 98·7$.

RUBIDIUM, IODIDE OF. RbI.—Obtained like the bromide, which it resembles in form. (Reissig.)

RUBIDIUM, OXYGEN-SALTS OF. The *acetate*, $C^2H^3RbO^2$, crystallises in nacreous laminæ (Grandeau). The *borate*, $Rb^2O.2B^2O^3.6H^2O$, separates from a hot solution of 2 at. boric acid and 1 at. rubidium-carbonate, at 6°, in small tabular rhombic crystals, exhibiting the combination $oP \,.\, \infty P \,.\, \infty\breve{P}\infty$, and having the angle $\infty P : \infty P = 82° 23'$; $\infty P : \infty\breve{P}\infty = 131° 4'$. It is permanent in the air, more soluble in hot than in cold water, and has an alkaline taste. (Reissig, Ann. Ch. Pharm. cxxvii. 33.)

Carbonates.—The *neutral salt*, Rb^2CO^3, is prepared by precipitating the sulphate with baryta-water, adding carbonate of ammonium to the filtrate, evaporating to dryness, and exhausting the residue with water. The solution yields, on evaporation, indistinct crystals of the hydrated salt, $Rb^2CO^3.H^2O$, soluble in alcohol, and having a strong alkaline reaction. The crystals, when heated, give off their water, and leave the anhydrous carbonate as a sandy powder, which melts at a higher temperature. On exposure to the air, it deliquesces, and is converted into the *acid carbonate*, $RbHCO^3$, which forms glassy prismatic crystals, permanent in the air, having a very faint alkaline reaction, a cooling, not caustic taste, and easily converted by heat into the neutral carbonate. (Bunsen and Kirchhoff.)

Chlorate, $RbClO^3$.—Prepared by mixing sulphate of rubidium and chlorate of barium in equivalent proportions. It forms very small white prisms, having the taste of chlorate of potassium, soluble in water to the amount of 2·8 per cent. at 4·7°, and 1 per cent. at 195°. (Reissig).

Perchlorate, $RbClO^4$.—Obtained by decomposing the carbonate with perchloric acid, and purified by repeated crystallisation from boiling water. It forms a sandy powder, composed of hard shining microscopic crystals. The crystals obtained by evaporation over oil of vitriol appear to be trimetric and isomorphous with perchlorate of potassium. They are anhydrous, permanent in the air, less soluble than perchlorate of potassium, and have a disagreeable, slightly saline taste. They melt easily, and decompose at a red heat into oxygen and chloride of rubidium. (Louguinine, *Traité de Chimie par Pelouze et Frémy*, 3^me ed. iii. 1419.)

Chromates.—The *neutral salt*, Rb^2CrO^4 or $Rb^2O.CrO^3$, is obtained by adding carbonate of rubidium to a solution of the dichromate. If is isomorphous with chromate of potassium, has an alkaline reaction, and forms a solution of a fine yellow colour.

The *acid chromate* or *dichromate*, $Rb^2O.2CrO^3$, forms hard, rather bulky crystals, exactly like the corresponding potassium-salt. It is easily prepared, either by supersaturating a hot solution of the carbonate with chromic acid, or by fusing the nitrate or carbonate with oxide of chromium, lixiviating, and evaporating. The mother-liquor ultimately deposits crystals of the neutral salt. (Grandeau, Ann. Ch. Phys. [3] lxvii. 155; Jahresb. 1863, p. 184.)

The *nitrate* and *oxalates* of rubidium have been already described. The *sulphates* and *tartrates* will be described under the respective acids.

RUBIHYDRAN. (Schunck, Phil. Mag. [4] xii. 200, 270.)—A substance having the composition of hydrated rubian, produced, together with rubianic acid and rubidehydran, by treating rubian with acid carbonate of barium. The brown-yellow filtrate, obtained as described at p. 125, is again mixed with baryta-water to separate any still undecomposed rubian; carbonic acid is once more passed into it, and the red flocks which separate on evaporation are removed. The filtrate mixed with basic acetate of lead, yields a red precipitate, which is to be washed, decomposed by cold dilute sulphuric acid, and treated with carbonate of lead to remove the excess of that acid. The precipitates are then removed; sulphydric acid is passed into the liquid; the sulphide of lead is separated by filtration; and the filtrate is evaporated.

Rubihydran is a brown-yellow, transparent gum, having a bitter taste, and becoming soft and moist on exposure to the air. It gives up its water only after prolonged heating over the water-bath, and then gives by analysis, 51·1 per cent. C and 6·0 H, agreeing approximately with the formula $C^{56}H^{78}O^{35} = 2C^{28}H^{34}O^{15}.5H^2O$. In other experiments, Schunck obtained numbers agreeing with the formulæ $C^{56}H^{78}O^{35}.3H^2O$ and $C^{56}H^{78}O^{35}.6H^2O$.

Rubihydran dissolves easily in water, but is not very soluble in alcohol. It is not altered by boiling phosphoric, oxalic, acetic, or tartaric acid; neither is it precipitated by any metallic salt except basic acetate of lead. With acids, alkalis, and chlorine, it yields the same products as rubian.

RUBINDENIC ACID. Syn. with Isamic Acid (iii. 403).

RUBINIC ACID. Also called *Rufocatechuic acid* (Svanberg, Ann. Ch. Pharm. xxiv. 215). When a solution of catechin in an alkaline carbonate is exposed to the air, the liquid gradually assumes a dark red colour, and then yields with hydrochloric acid, red, non-crystalline flocks of rubinic acid, which, however, is so unstable that it blackens even during washing and drying. When dried in a vacuum, and already altered, it gave by analysis 61·04 per cent. carbon and 4·21 per cent. hydrogen.

The rubinates are red and slightly soluble: their solutions blacken during evaporation. The *potassium-salt* may be isolated by saturating the red solution of catechin in potassic carbonate with acetic acid, till the rubinic acid begins to separate, adding alcohol to the filtrate, and drying the precipitated salt in a vacuum. It is very soluble in water; its solution forms red precipitates with metallic salts.

RUBIRETIN. $C^7H^6O^2$.—A substance, isomeric with benzoic acid, existing in madder-root, and obtained as a bye-product in the preparation of rubian (p. 123); in the decomposition of rubian by acids and by erythrozym (p. 124; also *Gmelin's Handbook*, xiv. 133, 135), and in the preparation 1 of rubiadin (p. 120); in the last case as a lead-compound. It is also produced by boiling chlororubian with alkalis.

The mixture of the lead-compounds of rubiretin and verantin, obtained in the preparation of rubiadin, yields, when decomposed by boiling hydrochloric acid, a brown powder, from which the rubiretin may be dissolved out by cold alcohol, the greater part of the verantin remaining behind. The alcoholic solution, when evaporated, leaves the rubiretin, which, if it does not melt in boiling water, must be purified by re-solution in cold alcohol and evaporation of the filtrate. A similar mode of purifying may be applied to rubiretin obtained as a secondary product under other circumstances.

Properties.—Rubiretin is a dark reddish-brown resin, brittle and friable in the cold, soft at 65°, melting, at about 100°, to dark-brown drops. It gives by analysis, 68·41 per cent. C, and 5·22 H (calc. 68·85 C, 4·91 H, 26·24 O).

Rubiretin dissolves sparingly in boiling *water*, but softens therein, and on cooling deposits yellow flocks, which increase on the addition of an acid. It is easily soluble in *alcohol*. It dissolves with dark orange colour in *oil of vitriol*, and is precipitated by water. It dissolves in *ammonia*, in the *pure fixed alkalis*, and in *alkaline carbonates*, forming brown-red solutions, from which it is precipitated by acids. The ammoniacal solution forms purple precipitates with *chloride of barium* and *chloride of calcium*, dirty red with *alum* and *nitrate of silver*. It dissolves in aqueous *ferric chloride*, with dark red-brown colour, and is precipitated by acids. When free from alizarin, it does not dye mordanted fabrics.

When heated in a test-tube, it generally yields a scanty sublimate of alizarin, together with a brown oil. It is decomposed by hot *oil of vitriol*. Boiling *nitric acid* converts it into a yellow substance, which no longer softens in boiling water, and is scarcely soluble in alcohol. *Chlorine* passed into the alcoholic solution of rubiretin, decolorises it, and renders it no longer precipitable by acids. (Schunck.)

RUBITANNIC ACID. Tannic acid from the leaves of *Rubia tinctorum*. (Willigk, Ann. Ch. Pharm. lxxxii. 340; Gm. xv. 532.)

RUBRINITRIC ACID, or *Nitro-hæmatic acid*. See Picramic Acid under Phenol (iv. 406).

RUBY. The Oriental ruby is a red variety of corundum (ii. 86); see also *Dana's Mineralogy* (ii. 111). The red varieties of spinel are sometimes called *Spinel ruby*, *Balas ruby*, or *Alamandin ruby*. (See Spinel.)

RUE, OIL OF. The essential oil obtained by distilling garden rue (*Ruta graveolens*) with water. When purified by a few rectifications, it is somewhat viscid; has a specific gravity of 0·837 at 18°; a strong disagreeable odour, like that of the plant; a slightly bitter aromatic taste; boils at 228°—230°; and solidifies, between + 1° and − 2°, to shining crystalline laminæ, resembling those obtained from anise-oil.

Oil of rue is chiefly a mixture of a hydrocarbon with an aldehyde or ketone belonging to the series $C^nH^{2n}O$. This compound, separable by alkaline bisulphites, was formerly regarded, according to the investigations of Gerhardt (Compt. rend. xxvi. 225, 361; *Traité*, ii. 773), and of Cahours (Compt. rend. xxvi. 262), as capric or rutic aldehyde, $C^{10}H^{20}O$. But Greville Williams (Phil. Trans. 1858, [1] 99; Jahresb. 1858, p. 443) has shown that the crude oil contains two such compounds, viz., $C^{11}H^{22}O$ and $C^{12}H^{24}O$, the latter in comparatively small quantity; and this result has been confirmed by Harbordt. (Ann. Ch. Pharm. cxxiii. 293; Jahresb. 1862, p. 250.)

Williams, by subjecting crude oil of rue to repeated fractional distillation, obtained distillates having boiling-points between 160° and 238°. The portion boiling between 160° and 188°, give, with alkaline bisulphites, scarcely traces of a crystalline compound; but the fractions of higher boiling-point yield crystalline compounds when thus treated (best with the ammonium-salt); and the portions boiling above 210° solidify, after a few hours' contact with the acid sulphite, to a crystalline mass, from which, after washing with the solution of the sulphite, pressure, &c., the aldehyde or ketone may be separated by distillation with potash.

The product thus obtained from the portion of the oil boiling between 210° and 232° is a colourless liquid, having a fruity odour quite different from that of rue. Specific gravity = 0·8497 at 15°. When cooled to + 7° and shaken, it solidifies to a white mass resembling camphor. Boils at 213° (oxidising at the same time unless kept in an atmosphere of hydrogen). Gives by analysis, 77·71 per cent. C and 13·07 H, agreeing with the formula $C^{11}H^{22}O$, which requires 77·65 C, 12·94 H, and 9·41 O. Vapour density, obs. = 5·870; calc. = 5·874. Williams regards this compound as euodic aldehyde or hydride of euodyl, $C^{11}H^{21}O.H$, the name being suggested by its fragrant odour. See also Hallwachs (Jahresb. 1859, p 506).

The higher fractions of crude oil of rue, yielded also by similar treatment a small quantity of a liquid boiling at 232°, and having nearly the composition of lauric aldehyde, $C^{12}H^{24}O$; anal. 78·1 per cent. C, 12·9 H; calc. 78·3 C, 13·0 H, and 8·7 O. Vapour-density, obs. = 6·182; calc. = 6·366.

According to Harbordt (*loc. cit.*), the compound $C^{11}H^{22}O$, which forms the chief constituent of rue-oil, is not euodic aldehyde, but a ketone, viz., methyl-caprinol = $C^{10}H^{19}O.CH^3$. The portion of the crude oil boiling at 228°, yielded by analysis numbers agreeing with the formula of lauric aldehyde, $C^{12}H^{24}O$; but the compound obtained therefrom with acid ammonium-sulphite, gave by distillation with carbonate of sodium, a body agreeing nearly in composition and vapour-density (obs. 6·03) with the formula $C^{11}H^{22}O$. This 11-carbon compound yielded by oxidation (together with oxalic acid), capric acid, caprylic acid, and lower members of the acetic acid series, but no acid containing 11 at. carbon.

The portion of rue-oil which does not combine with alkaline bisulphites, is separable into a more volatile portion, having the composition of turpentine oil, and a less volatile portion, which appears to be isomeric with borneol, but boils at a lower temperature. (Gr. Williams.)

RUFIGALLIC ACID. $C^7H^4O^4.H^2O$. *Para-ellagic acid.* (Robiquet, Ann. Ch. Pharm. xix. 204.)—This acid, which, in the dry state, contains the elements of gallic acid *minus* 1 at. water, is produced by gently heating gallic acid to 140° with 5 pts. of strong sulphuric acid, and pouring the sticky mass when cold into cold water, drop by drop. An abundant red-brown precipitate is then formed, partly flocculent, partly crystalline, and the crystalline portion, which amounts to 50 or even 70 per cent. of the gallic acid employed, may be separated by levigation.

Rufigallic acid thus obtained forms kermes-brown crystalline grains, which at 120° give off 10·6 per cent. (1 at.) water, and lose their lustre. When strongly heated in the air, it carbonises in great part, becoming covered with small cinnabar-coloured prisms. It dissolves in 3,500 pts. of water, easily in potash, the solution, when exposed to the air, depositing coloured crystals after a long time. On boiling the acid with stuffs mordanted with alum or an iron-salt, dyes are obtained similar to those produced by madder, but less bright.

RUFIMORIC ACID. (Wagner, J. pr. Chem. li. 82.)—An acid obtained, in the form of a dark brick-red precipitate, when a solution of morintannic acid in cold strong sulphuric acid, or that produced by boiling morintannic acid with dilute hydrochloric acid, is left to itself for some time. When purified by washing with cold water, solution in alcohol, reprecipitation with water, and drying, it forms a dark-red amorphous powder, very soluble in alcohol, less soluble in water, very slightly soluble in ether. A very small quantity of ammonia suffices to render it soluble in water, in all proportions. Its solutions have an acid reaction. Its composition, as determined by analysis (54·4 per cent. C, 4·4 H), is very near to that of morintannic acid; and as the latter can be reproduced by the action of alkalis on rufimoric acid, it is probable that the two acids are either isomeric, or differ only by the elements of water.

Rufimoric acid may be heated without decomposition to 130°; but above that temperature, it gives off vapours which condense to a crystalline mass, exhibiting all the characters of pyrocatechin. It dissolves with red colour in strong sulphuric acid without alteration, also in hydrochloric acid. Nitric acid converts it into oxalic acid and a nitrogenised acid. With caustic alkalis and their carbonates, it forms crimson solutions, which lose their colour but slowly. An alcoholic solution of the acid forms with alcoholic potash a dark-red viscous precipitate. Rufimoric acid, boiled with potash or baryta, is reconverted into morintannic acid.

The aqueous solution of rufimoric acid (containing a trace of ammonia), does not precipitate alum; but on adding more ammonia, a dark-red lake is thrown down. The same reaction is produced with stannous chloride and chloride of barium. Neutral acetate of lead, cupric acetate, and mercurous nitrate form red or brown precipitates. Nitrate of silver and sulphate of zinc are not precipitated.

Chlorine decomposes the solution of rumiforic acid, throwing down red flocks.

RUFIN. $C^{21}H^{20}O^{8}$. (Mulder, Rev. scientif. iii. 50.)—A compound produced by the action of heat on phlorizin, and differing therefrom by the elements of 2 at. water: $C^{21}H^{24}O^{10} = C^{21}H^{20}O^{8} + 2H^{2}O$. It is a resinous substance of a red colour, very friable, dissolving in alcohol with deep orange colour, nearly insoluble in ether. Water dissolves it at the boiling heat, and decolorises it instantly; the solution becomes milky on cooling. Rufin dissolves in strong sulphuric acid, producing a fine red solution, which is decolorised by water. It is insoluble in hydrochloric acid; decomposed by hot nitric acid. It dissolves with red colour in potash and ammonia, and is precipitated therefrom by acids.

RUM. A spirituous liquor distilled in the West Indies from molasses. (See *Ure's Dictionary of Arts, &c.* iii. 606.)

RUMICIN. Syn. with CHRYSOPHANIC ACID (i. 958). This substance exists in the roots of various species of *Rumex*, viz., *Rumex patientia*, *R. palustris*, *R. acutus*, *R. aquaticus*, and *R. Hydrolapathum*, as well as in rhubarb and wall-lichen.

RUSIOCHINE. A red substance produced by the action of chlorine-water and ammonia on quinine (p. 18).

RUTAMIDE. Syn. with CAPRAMIDE.

RUTHENHYPERIC ACID. See RUTHENIUM, OXIDES OF (p. 137).

RUTHENIOCYANIDES. See CYANIDES OF RUTHENIUM (ii. 271).

RUTHENIUM. *Atomic weight*, 104. *Symbol*, Ru.—This metal, discovered by Claus in 1846, occurs in platinum-ore, and chiefly in osmiridium, which sometimes contains it to the amount of 3 to 6 per cent. Its properties and combinations have been examined chiefly by Claus (Pogg. Ann. lxiv. 192, 624; lxv. 200; Ann. Ch. Pharm. lvi. 257; lix. 234; lxiii. 259), Frémy (*Traité de Chimie par Pelouze et Frémy*, 3^{me} ed. iii. 1334), and Deville and Debray (Ann. Ch. Phys. [3] lvi. 385; Jahresb. 1859, p. 233).

Extraction: 1. Pulverised osmiridium, mixed with about half its weight of common salt, is heated to low redness in a current of moist chlorine; the disintegrated mass is digested in cold water; and the concentrated solution, which is brown-red and almost opaque, is mixed with a few drops of ammonia and gently heated, whereupon it deposits a copious black-brown precipitate, consisting of sesquioxide of ruthenium and dioxide of osmium. This precipitate, after being washed with nitric acid, is heated in a retort, till the osmium is expelled in the form of osmic tetroxide. The residue is then ignited for an hour in a silver crucible with caustic potash free from silica, and the ignited mass is softened and dissolved by cold distilled water. The solution is left in a corked bottle for two hours to clarify; after which the perfectly transparent orange-coloured liquid is separated by a siphon, and neutralised with nitric acid. It then deposits velvet-black sesquioxide of ruthenium, which, when washed, dried, and ignited in an atmosphere of hydrogen, yields the pure metal. (Claus; see also PLATINUM-ORE, iv. 681).

2. Pulverised osmiridium is heated with 3 pts. peroxide and 1 pt. nitrate of barium; the mass is treated in the manner described under IRIDIUM (iii. 315, No. 5); and the orange-yellow solution of ruthenate of potassium, ultimately obtained by fusing the mixture of iridium and ruthenium with nitre and caustic potash, and lixiviating with water, is treated with carbonic or nitric acid till it becomes colourless; it then deposits oxide of ruthenium, slightly contaminated with silica. This oxide, strongly calcined in a graphite crucible, yields metallic ruthenium, which is then fused in the oxyhydrogen furnace (iv. 313). The ruthenium thus obtained still requires to be purified by one or more fusions with nitre and potash, till its density is brought up to 11·3. (Deville and Debray.)

3. Scaly osmiridium, consisting almost entirely of osmium, iridium, and ruthenium, is heated to bright redness in a porcelain tube, through which a current of air (freed from carbonic acid by passing through potash, and from organic matter by passing through oil of vitriol) is drawn by means of an aspirator. The osmium and ruthenium are thereby oxidised, the former being carried forward as tetroxide and condensed in caustic potash solution, while the oxide of ruthenium remains behind, together with iridium; and by fusing this residue with hydrate of potassium, and treating the

mass with water, a solution of potassic rutheniate is obtained as above (Frémy). According to Deville and Debray, the ruthenium thus obtained is still contaminated with small quantities of osmium, rhodium, and iridium.

Properties.—Ruthenium obtained by calcining one of its ammoniacal chlorides, is a white spongy mass; when separated from its oxides by reduction with hydrogen, it forms porous fragments, very much resembling iridium, and moderately easy to pulverise. It is the most refractory of all metals except osmium. Deville and Debray have, however, fused it by placing it in the hottest part of the oxyhydrogen flame at about 2 millimetres from the orifice of the jet. After fusion, it has a density of 11 to 11·4; that of the porous metal is only 8·6.

Ruthenium is scarcely attacked by nitromuriatic acid. It is, however, more easily oxidised than platinum, or even than silver (Frémy). When pure it is easily oxidised by fusion with hydrate of potassium, still more easily on addition of a small quantity of nitrate or chlorate, producing rutheniate of potassium, which dissolves in water, with orange-yellow colour.

RUTHENIUM, ALLOYS OF. Zinc forms with ruthenium an alloy, which crystallises in regular hexagonal prisms, takes fire when heated in the air, and burns with faint deflagration.

An alloy of tin and ruthenium, $RuSn^2$, is easily obtained by heating ruthenium to redness in a graphite crucible, with 10 to 15 times its weight of tin, and dissolving out the excess of tin from the cooled mass with hydrochloric acid. The alloy then remains in magnificent cubic crystals, like those of melted bismuth. (Deville and Debray.)

RUTHENIUM, CHLORIDES OF. Ruthenium forms three chlorides, viz., $RuCl^2$, $RuCl^3$, and $RuCl^4$; the last, however, is known only in combination.

The *dichloride*, $RuCl^2$, is produced, together with the trichloride, by igniting pulverised ruthenium in a stream of chlorine, the trichloride then volatilising; while the dichloride remains in the form of a black crystalline powder, insoluble in water and in all acids, even nitromuriatic acid, and only partially decomposed by alkalis. A soluble dichloride is formed by passing sulphydric acid gas into a solution of the trichloride. A brown sulphide is then precipitated, and the solution acquires a fine blue colour. If the excess of sulphydric acid be expelled by a current of air, a pure solution of the dichloride will be obtained, which becomes green by strong concentration, and yields with ammonia a green precipitate of the soluble dichloride (? hydrated). Both the blue and the green dichloride are converted into trichloride when heated with nitric acid.

Trichloride or *Ruthenious Chloride*, $RuCl^3$. Prepared by precipitating a solution of potassic rutheniate with an acid, dissolving the precipitated black oxide in hydrochloric acid, and evaporating. It is a yellow-brown, crystalline, very deliquescent mass, becoming dark-green and blue at certain points when strongly heated. It dissolves easily in water and in alcohol, leaving a small quantity of a yellow insoluble salt.

The concentrated solution of ruthenious chloride, mixed with concentrated solutions of the chlorides of potassium and ammonium, yields the double salts $K^2Ru'''Cl^5 = 2KCl.RuCl^3$ and $(NH^4)^2Ru'''Cl^5$, in the form of crystalline precipitates, with violet iridescence, very slightly soluble in water, insoluble in alcohol. The solution of the potassium-salt, left for some time in contact with water, becomes turbid and black, and deposits a black oxychloride of ruthenium; the same decomposition takes place immediately on heating the solution.

Tetrachloride of Ruthenium or *Ruthenic Chloride*, $RuCl^4$, is known only in its double salts. The *potassium-salt*, $K^2Ru^{iv}Cl^6 = 2KCl.RuCl^4$, is prepared by mixing a solution of ruthenic hydrate in hydrochloric acid with chloride of potassium, and evaporating to the crystallising point. It is brown, with rose-coloured iridescence, very soluble in water, but insoluble in alcohol. It appears to be dimorphous, inasmuch as, when deposited from a solution containing several other salts, it crystallises in microscopic six-sided prisms, but, under other circumstances, in regular transparent octahedrons, being then isomorphous with the corresponding salts of platinum, palladium, osmium, and iridium.

The *ammonium-salt*, $2NH^4Cl.RuCl^4$, is obtained like the potassium-salt, which it resembles closely.

RUTHENIUM, CYANIDES OF. (See CYANIDES, ii. 271.)

RUTHENIUM, DETECTION AND ESTIMATION OF. Ruthenium is most frequently met with in solution in the form of trichloride. This solution, which is of an orange-yellow colour, is distinguished by its character of decomposing, when heated, into hydrochloric acid and blackish-brown sesquioxide of ruthenium. The same solution exhibits with reagents the following characters:—

Sulphydric acid partly precipitates the ruthenium in the form of a black sulphide, but at the same time reduces the trichloride to dichloride, the reduction being attended with a change of colour from orange-yellow to a fine azure-blue: this reaction is extremely delicate, and very characteristic of ruthenium. *Zinc* effects the same reduction. *Sulphydrate of ammonium* throws down the greater part of the ruthenium, in the form of a black-brown sulphide, not perceptibly soluble in excess.—The *caustic alkalis, alkaline carbonates*, and *phosphate of sodium* precipitate the black sesquioxide, insoluble in excess of the reagent.—*Borax* forms no precipitate at first, but, on heating the solution, the hydrated sesquioxide is thrown down.—*Sulphurous acid, oxalic acid*, and *formate of sodium* do not precipitate the metal, but merely decolorise the solution. —*Ferrocyanide of potassium* decolorises the solution at first, but afterwards turns it bluish-green.—*Sulphocyanate of potassium* produces, after awhile, a red coloration passing to deep red-purple, and changing to a fine violet on heating the liquid. This is one of the most characteristic reactions of ruthenium, inasmuch as soluble sulphocyanates do not exhibit any very decided character with the other metals of the platinum group; for its distinct production, however, it is necessary that the solution be free from other platinum-metals.—*Acetate of lead* forms a purple-red precipitate, inclining to black.—*Cyanide of mercury* colours the solution blue, and throws down a blue precipitate.—*Nitrate of silver* forms a black precipitate, which is a mixture of chloride of silver and sesquioxide of ruthenium; the oxide dissolves, after a while, in the nitric acid, leaving a white residue of chloride of silver; and if ammonia be then added in excess, the chloride of silver dissolves, and the sesquioxide of ruthenium is reprecipitated: this is also a very delicate reaction.—The *chlorides of potassium* and *ammonium* throw down, from concentrated solutions, crystalline precipitates of double chlorides, exhibiting a play of colours inclining to violet.—The *nitrites of the alkali-metals* form with ruthenious solutions, double salts $[3MNO^2.Ru'''(NO^2)^3]$, which dissolve readily in excess of the alkaline nitrite, forming solutions, which, when treated with a small quantity of yellow sulphide of ammonium, assume a splendid dark-red colour, changing to brown without precipitation of sulphide. This reaction is recommended by Gibbs and by Claus (Jahresb. 1863, p. 697) for the detection of nitrites.

The solution of chlororutheniate of potassium, $2KCl.RuCl^4$, exhibits the following reactions:—With *sulphydric acid*, no reaction at first; but after a while, or on heating, a brown precipitate of disulphide, RuS^2. a considerable quantity of ruthenium, however, remaining in solution.—Yellow *sulphydrate of ammonium* immediately throws down part of the ruthenium, in the form of a brown-yellow sulphide; the reaction is complete on the addition of an acid.—*Potash* and *alkaline carbonates* form no precipitate in the cold; a deposition of oxide takes place on heating the liquid, but a considerable portion still remains dissolved.—*Nitrate of silver* forms a rose-coloured, mercurous *nitrate*, a light-yellow, and *stannous chloride* a yellow precipitate.

The compounds of ruthenium may readily be distinguished from those of the other platinum-metals, by fusing a few milligrammes of the substance in a platinum-spoon, with a large excess of nitre, leaving it to cool when it ceases to froth, and dissolving the cooled mass in a little distilled water. An orange-yellow solution of potassic rutheniate is thus formed, which, on addition of a drop or two of nitric acid, yields a bulky black precipitate; and on adding hydrochloric acid to the liquid, with the precipitate still in it, and heating it in a porcelain crucible, the oxide dissolves, forming a solution which has a fine orange-yellow when concentrated, and when treated with sulphydric acid till it becomes nearly black, yields a filtrate of a splendid sky-blue colour. Characteristic reactions are also obtained with sulphocyanate of potassium and acetate of lead.

Metallic ruthenium may be distinguished from the other platinum-metals by mixing it with common salt, and igniting the mixture in a current of chlorine. The resulting black mass dissolves in water, with a fine orange-yellow colour, which of itself is sufficient to distinguish ruthenium from rhodium and iridium (the former of which yields under similar circumstances a rose-coloured, and the latter a black-brown solution). It may be further distinguished by the black precipitate which it yields with ammonia, and by the reactions with sulphydric acid, &c., above mentioned.

Estimation and Separation.—Ruthenium is precipitated from its solutions in the form of oxide, and generally as sesquioxide, viz., from a solution of the sesquichloride, either by alkalis or by simply heating the solution, and from a solution of rutheniate of potassium by nitric acid. The precipitated oxide is reduced to the metallic state by ignition in an atmosphere of hydrogen. As, however, the precipitate generally contains alkali, which cannot be removed by washing, the reduced mass must be treated with water; the liquid filtered from the ruthenium; and the metal, before weighing, must be again ignited, and left to cool in an atmosphere of hydrogen, as it oxidises when heated in the air.

Ruthenium has hitherto been found only associated with the metals of the platinum-residues, and from these it is separated by the methods already described (p. 134; see also PLATINUM-ORE, iv. 681).

The following methods of separating ruthenium from platinum, rhodium, and iridium, are given by Gibbs (Sill. Am. J. [2] xxxiv. 341; Jahresb. 1863, p. 292):—

1. From *Platinum.*—The mixture of the double chlorides, K^2PtCl^6 and K^2RuCl^6, is treated with a cold solution of chloride of potassium; the resulting solution, which contains chiefly the ruthenium-salts, is heated with nitrite of potassium, and evaporated to dryness; and the residue is treated with hot absolute alcohol, which leaves chloroplatinate of potassium undissolved. The alcoholic solution containing the chlororutheniate of potassium (together with traces of platinum) is evaporated; the residue is heated with hydrochloric acid; the deep rose-coloured solution of the potassic chlororutheniate is repeatedly evaporated to dryness with sal-ammoniac; and the hot aqueous solution of the resulting chlororutheniate of ammonium is converted, by evaporation with ammonia, into the yellow ammonio-chloride, $4NH^3.RuCl^2.3H^2O$. The latter, when dissolved in hot water, yields with mercuric chloride a yellow crystalline precipitate of the salt, $4NH^3.RuCl^2.Hg''Cl^2$, which may be freed from platinum by recrystallisation, and yields by ignition silver-white ruthenium.

2. A similar method serves for the separation of ruthenium from *rhodium*, the latter metal remaining undissolved as chlororhodiate of potassium, when the solution of the two double chlorides is treated with nitrite of potassium, and the evaporated residue with alcohol. The chlororhodiate of potassium is then either converted into metallic rhodium by ignition with sal-ammoniac, or dissolved in hot hydrochloric acid, supersaturated with ammonia, and precipitated as sulphide by sulphydric acid. (Gibbs.)

3. From *Iridium.*—The best mode of proceeding is to heat the solution of the two metals with an excess of nitrite and carbonate of sodium till a light orange-yellow is produced; then add sulphide of sodium by small portions, till part of the precipitated sulphide of ruthenium is redissolved; boil for a few minutes; and mix the liquid, after cooling, with a slight excess of hydrochloric acid. The precipitated sulphide of ruthenium is washed with hot water, dissolved in nitromuriatic acid, and converted, first into chlororutheniate of ammonium, then into the above-mentioned mercury-compound. The solution filtered from the sulphide of ruthenium, and evaporated with hydrochloric acid and sal-ammoniac, yields pure chloriridiate of ammonium.—The tetrachlorides of iridium and ruthenium may also be separated by heating with nitrite and carbonate of potassium, evaporating to dryness, and treating the residue with absolute alcohol. The ruthenium-salt then dissolves, whilst the iridium-salt remains, and may be easily converted into chloriridiate of ammonium.

According to Gibbs, the separation of iridium and ruthenium by ignition with nitre and potash does not yield good results, inasmuch as part of the ruthenium always remains unattacked, and a small quantity of the iridium dissolves, together with the rutheniate of potassium.

On the separation of ruthenium and the other platinum-metals, see further Gibbs (Sill. Am. J. [2] xxxvii. 57; Jahresb. 1864, p. 288; Bull. Soc. Chim. 1864, ii. 38), Carey-Lea (Sill. Am. J. [2] xxxviii. 31; Jahresb. 1864, p. 290).

Atomic Weight of Ruthenium.—Claus (J. pr. Chem. xxxiv. 173, 420; Ann. Ch. Pharm. lvi. 257), by the analysis of chlororuthenite of potassium, $2KCl.RuCl^3$, found that the atomic weight of the metal was 104·22, which is nearly the same as that of rhodium. Other experiments gave higher numbers, but the above determination is generally regarded as nearest to the truth.

RUTHENIUM, OXIDES OF. Ruthenium forms five oxides, viz. RuO, Ru^2O^3, RuO^2, RuO^3, and RuO^4, the fourth, however, being known only in combination.

The *protoxide*, RuO, obtained by calcining the dichloride with carbonate of sodium in a current of carbonic anhydride, and washing the residue with water, has a dark-grey colour and metallic lustre, is not acted upon by acids, but is reduced by hydrogen at ordinary temperatures.

Sesquioxide, or *Ruthenious Oxide*, Ru^2O^3.—Pulverised ruthenium, heated in contact with the air, rapidly absorbs 48 per cent. oxygen, and is afterwards slowly converted into the anhydrous sesquioxide, which has a deep blue colour, is insoluble in acids, and is reduced when heated into hydrogen gas.

The hydrated sesquioxide, $Ru^2O^3.3H^2O = RuH^3O^3$, is obtained as a blackish-brown precipitate, when a solution of ruthenious chloride is treated with an alkaline carbonate. This hydrate, after prolonged washing, still retains 3 or 4 per cent. of alkali; it dissolves with yellow colour in acids, but is not dissolved by water or by alkalis. When strongly heated in an atmosphere of carbonic anhydride, it gives off its water, and becomes insoluble in acids.

The *dioxide* or *ruthenic oxide*, RuO^2, is formed by roasting the disulphide, or by strongly igniting ruthenic sulphate, RuS^2O^8 or $RuO^2.2SO^3$. The former method yields a black-blue powder with a tinge of green; the latter, grey particles with metallic lustre, and bluish or greenish iridescence.

The *hydrate*, $RuH^4O^4 = RuO^2.2H^2O$, is obtained as a gelatinous precipitate, by decomposing chlororutheniate of potassium with carbonate of sodium, or ruthenic sulphate with caustic potash or soda; in the latter case, however, the solution must be evaporated, as it retains a considerable quantity of the hydrate. Ruthenic hydrate, when dried and heated in a platinum spoon, deflagrates with vivid incandescence, and is scattered about. It dissolves in acids, forming yellow solutions. The solution in hydrochloric acid turns red when evaporated, and ultimately leaves red-brown ruthenic chloride. The hydrate dissolves also with light-yellow colour in alkalis.

The *trioxide*, RuO^3, commonly called *ruthenic acid*, is known only in the form of a potassium-salt, which is obtained by igniting ruthenium with a mixture of potash and nitrate or chlorate of potassium. It dissolves in water, forming an orange-yellow solution, which has an astringent taste, colours organic substances black by coating them with oxide, and is decomposed by acids, yielding a precipitate of the sesquioxide.

Tetroxide of Ruthenium, RuO^4. *Ruthenic tetroxide. Perruthenic acid. Ruthenhypersäure.*—This volatile oxide, analogous to osmic tetroxide, is obtained by heating to dull redness, in a silver crucible, a mixture of 3 grammes of ruthenium with 24 grms. caustic potash and 8 grms. nitre, dissolving the fused mass in 48 grms. of water, introducing the solution into a tubulated retort connected by a long condensing tube with a flask containing caustic potash, and passing chlorine into the liquid. The liquid becomes hot, and the tetroxide passes over, condensing in the neck of the retort and the tube, as a golden-yellow crystalline crust, which melts between 50° and 60°. Part of it, however, remains in the liquid, and may be separated by distillation. To purify it from adhering water and chlorine, it is melted in a tube under a layer of water; it then crystallises on cooling, and may be pressed between paper.

Ruthenic tetroxide is a golden-yellow, crystalline mass, in which rhomboïdal prisms may be distinguished. It is heavier than sulphuric acid, very volatile, vaporising even at ordinary temperatures, and emitting an odour like that of nitrous acid; melts at 58°, forming a yellow liquid, which boils at about 100°. It dissolves sparingly in water, the solution remaining unaltered in the dark, but decomposing rapidly even in diffused daylight. It dissolves in hydrochloric acid, without losing its characteristic odour, and on adding alcohol to the solution, trichloride of ruthenium is formed. Sulphurous acid colours the solution of ruthenic tetroxide red-purple, changing to violet-blue when heated. Sulphydric acid throws down a black precipitate of oxysulphide. The dry oxide moistened with strong potash, becomes hot, melts, and volatilises in great part, the rest gradually dissolving as rutheniate of potassium. (Claus, J. pr. Chem. lxxix. 28; Jahresb. 1859, p. 260.)

RUTHENIUM, SULPHIDES OF. Sulphydric acid, passed into a solution of either of the chlorides of ruthenium, usually forms a precipitate consisting of sulphide and oxysulphide of ruthenium mixed with free sulphur. The blue solution of the protochloride yields a dark-brown sesquisulphide, Ru^2S^3. When sulphydric acid gas is passed for a long time into a solution of the trichloride, disulphide of ruthenium, RuS^2, is formed, as a brown-yellow precipitate, becoming dark-brown by calcination.

RUTHENIUM-COMPOUNDS, AMMONIACAL. *a. Di-ammoniacal.*—The *oxide*, $RuO.2NH^3$, is obtained by evaporating a solution of the tetrammoniacal oxide, $RuO.4NH^3$, in a dry vacuum, as a yellowish-brown spongy mass, formed of small, very deliquescent, crystalline laminae, containing 5 at. water. When placed on the tongue, it exerts a caustic action, stronger even than that of potash. Its salts resemble those of the following series, excepting that they are of a darker colour:—

β. Tetrammoniacal.—The *chloride*, $RuCl^2.4NH^3.3H^2O$, is obtained by dissolving 1 pt. of chlororutheniate of ammonium, $2NH^4Cl.RuCl^4$, in 16 pts. of water, boiling the solution for an hour with 30 pts. of caustic ammonia and 1 pt. of ammonium-carbonate, evaporating to dryness over the water-bath, digesting the pulverised crystalline mass with 1 pt. of water, and washing it on a filter with weak alcohol, till the free sal-ammoniac is completely dissolved. The salt when dry is dissolved in 4 pts. of hot water containing a little carbonate of ammonium; and the solution, filtered while still hot, deposits the salt on cooling in beautiful golden-yellow, oblique rhombic crystals, which are not very soluble in cold water, and quite insoluble in alcohol. The crystals retain their water till they are heated to a temperature at which they undergo complete decomposition, leaving metallic ruthenium. The solution has a strong tendency to form slightly soluble compounds with other metallic salts. Caustic potash does not eliminate ammonia from it at ordinary temperatures, but liver of sulphur immediately sets ammonia free; with chloride of platinum, it immediately forms a precipitate of the compound $RuCl^2.4NH^3.PtCl^4$.

The chloride, treated with oxide of silver, yields the oxide $RuO.4NH^3$, which, however, has not been obtained in the solid state, as its solution when evaporated gives off half its ammonia, leaving the oxide $RuO.2NH^3$, already described. The solution of the tetrammoniacal oxide resembles that of potash; it absorbs carbonic acid from the air, expels ammonia from its salts, precipitates metallic oxides, and dissolves alumina: it does not, however, exert any action on the salts of copper or silver.

The oxygen-salts of this base, obtained by decomposing the chloride with the corresponding silver-salts, are very soluble in water, but, for the most part, insoluble in alcohol. The *carbonate*, $RuCO^3.2NH^3.5H^2O$, is soluble, strongly alkaline, and crystallises in light-yellow rhombic prisms. The *nitrate*, $Ru(NO^3)^2.2NH^3.2H^2O$, forms small rhomboïdal prisms, having a sulphur-yellow colour and strong lustre, melts when heated, and decomposes with slight detonation. The *sulphate*, $RuSO^4.2NH^3.4H^2O$, crystallises in fine transparent rhombic plates of a golden-yellow colour. When exposed to the air, they give off part of their water, and become opaque, acquiring a metallic aspect. (Claus, J. pr. Chem. lxxix. 28; lxxxv. 129; Jahresb. 1859, p. 263; 1861, p. 320.)

RUTHERFORDITE. A mineral from the gold-mines of Rutherford County, North Carolina, where it occurs in small, brown, monoclinic crystals, which exhibit incandescence when heated. According to Shepard (Sill. Am. J. xii. 209), it contains titanic oxide and ceric oxide; according to T. S. Hunt (*ibid.* [2] xiv. 344), 58 per cent. titanic oxide, 12 lime, &c.

RUTIC ACID. Syn. with CAPRIC ACID (i. 742).

RUTILE. A variety of native titanic oxide. (See TITANIUM.)

RUTILIN. The name applied by Braconnot to a red resinous substance (called *olivin* by Mulder), produced by salicin with strong sulphuric acid: probably impure saliretin.

RUTIN. $C^{25}H^{28}O^{15}$. *Rutinic Acid. Phytomelin. Melin. Vegetable Yellow.* (Weiss, Pharm. Centr. 1842, p. 903.—Borntrӓger, Ann. Ch. Pharm. liii. 385.—Rochleder and Hlasiwetz, *ibid.* lxxxii. 197.—W. Stein, J. pr. Chem. lviii. 399; lxxxviii. 280.—Hlasiwetz, Ann. Ch. Pharm. xcvi. 123; further, Chem. Centr. 1862, p. 449.—Zwenger and Dronke, Ann. Ch. Pharm. cxxiii. 145.—Gm. xvi. 500.)—A glucoside, which appears to be very widely diffused in the vegetable kingdom. It was first obtained from garden rue, by Weiss and by Borntrӓger; afterwards from capers, the flower-buds of *Capparis spinosa*, by Rochleder and Hlasiwetz, also by Zwenger and Dronke; and from the so-called *Waifa*, the undeveloped flower-buds of *Sophora japonica*, by Stein and by W. Martius (N. Jahrb. Pharm. i. 241). According to Stein, safflower yellow is uncrystallisable rutin; the colouring matters of straw and of *Æthalium*, *Hippophaë*, and *Polygonum Fagopyrum* likewise agree in character with rutin.

Preparation: 1. *From Garden rue.*—The dried and comminuted plant is boiled for half-an-hour with common vinegar, and the expressed liquid is set aside for several weeks, or so long as it continues to deposit impure rutin. The deposit is washed with cold water, heated to boiling with 4 pts. of acetic acid and 16 pts. of water, filtered, and left for some days to crystallise. The crystals obtained thus, and by partial evaporation of the mother-liquor, are dissolved in 6 pts. of boiling water; the solution is treated with animal charcoal; and, after addition of $\frac{1}{8}$ of water, the alcohol is distilled off. The rutin crytallises from the residue after some days, the more readily the less strongly the solution has been heated (Borntrӓger, Weiss). A green resin with which the rutin is contaminated is difficult to remove by crystallisation; it is more easily got rid of by acidifying the alcoholic solution with acetic acid, and precipitating with neutral acetate of lead. On removing the lead from the filtrate by sulphydric acid, and evaporating, the rutin crystallises, and may be recrystallised from boiling water. It still contains a substance resembling coumarin, from which it may be freed, though with great difficulty, by repeated boiling with ether. (Zwenger and Dronke.)

2. *From Preserved Capers.*—The capers are macerated in water for a few hours, after which the water is poured off, and the capers are pressed; this process is repeated twice, to remove salt and vinegar. The decoction, obtained by twice boiling the washed capers in not too large a quantity of water, throws down, on standing for 24 hours, a

large quantity of yellowish-white flocks, which are collected, dried, and dissolved in boiling alcohol, whereby a gelatinous substance is left undissolved. The alcoholic solution is mixed with water, and the alcohol is distilled off; the residue then solidifies on cooling, from crystallisation of rutin. The crystals are purified by pressing and recrystallisation from boiling water (Rochleder and Hlasiwetz). Zwenger and Dronke add to the solution in hot water a few drops of solution of neutral acetate of lead (too much would precipitate a compound of rutin and lead-oxide), and free the filtrate from lead by means of sulphydric acid.

3. *From Waifa.*—The coarsely-bruised waifa is repeatedly boiled with alcohol of 80 per cent., and the greater part of the alcohol is distilled off, whereupon the residue thickens to a pulp of impure rutin, amounting to 11 per cent. of the waifa employed. It is crystallised repeatedly from boiling water, and afterwards washed with cold water (Stein). To purify the rutin, hydrate of lead is added to the boiling alcoholic solution, so long as it is coloured brown; the solution is filtered; and the rutin is thrown down from the filtrate by an additional quantity of lead-hydrate. The latter pure yellow precipitate is decomposed by alcoholic sulphydric acid, and the filtrate is free from sulphide of lead, and evaporated to crystallisation. (Stein.)

Properties.—Rutin crystallises from its aqueous solution in pale yellow-delicate needles, probably having the composition $2C^{25}H^{28}O^{15}.5H^2O$. It has a slightly styptic, afterwards saline taste. The crystals, heated to 100°, give off from 1·61 to 2·12 water, and leave a hydrate containing $C^{25}H^{28}O^{15}.2H^2O$ (mean of analyses, 49·51 C, 5·47 H, 45·02 O; calc. 49·66 C, 5·29 H, 45·05 O), which, at 150° to 160°, gives off its 2 at. water (5·63—5·92 per cent.), and leaves anhydrous rutin, $C^{25}H^{28}O^{15}$, containing 52·66 C, 5·02 H, 42·32 O (calc. 52·81 C, 4·93 H, 42·27 O). (Zwenger and Dronke.)

Rutin is nearly insoluble in cold but dissolves easily in boiling water, forming a pale-yellow solution, which is decolorised by acids, and quickly deposits the rutin on cooling. It dissolves slightly in cold absolute alcohol, freely in boiling alcohol of 76 per cent., and crystallises therefrom only on concentration and addition of water. It is insoluble in boiling *ether*. It dissolves freely in hot *acetic acid*, and is partially deposited on cooling. By digestion with moderately dilute mineral acids, it acquires a lemon-yellow colour, and is rendered paler again by water; when heated with acids, it dissolves and suffers decomposition (*infra*). It absorbs *hydrochloric acid gas*. (Stein.)

Rutin dissolves easily in *alkalis* and *alkaline carbonates*—also in *baryta-*, *strontia-*, and *lime-water*, forming yellow solutions, which deposit the rutin unaltered on addition of acids, and turn brown in the air from absorption of oxygen. According to Stein, it decomposes *carbonate of sodium* and *ferrocyanide of potassium*. It is coloured dark-green by *ferric chloride*, brown-red to greenish by *ferrous chloride*. *Acetate of lead*, added to an alcoholic solution of rutin, or in excess to aqueous rutin, forms a yellow precipitate containing $C^{25}H^{28}O^{15}.2Pb''O$. (Borntrӓger; Rochleder and Hlasiwetz.)

Decompositions.—1. Rutin, after dehydration at 160°, cakes together at 190°, and then melts to a yellow viscid liquid, which, on cooling, solidifies to an amorphous mass, and takes up water when immersed in it. When more strongly heated it is carbonised, emitting an odour of caramel, and yielding a distillate containing quercetin (Zwenger and Dronke). Rutin, melted at 180°, forms a yellow viscid liquid on cooling, and partly crystallises; at 220° a yellow sublimate is produced (Borntrӓger). Over a bath of oil of vitriol, rutin becomes coloured at 100°, melts at 120°, giving off gas-bubbles, boils at 200°, and is decomposed at 290°, yielding products of distillation. The water evolved at 200° over the oil-bath contains formic acid; a solution of the melted mass in a little boiling water throws down amorphous quercetin on standing (Stein).—2. *Nitric acid* boiled with rutin produces chiefly oxalic acid (Zwenger and Dronke). According to Stein, it forms picric acid with a trace of oxalic acid. Cold nitric acid colours rutin yellow, then quickly olive, and at last red-brown (Stein).—3. Rutin forms with *oil of vitriol* a brown-yellow (olive-green, according to Rochleder and Hlasiwetz), afterwards brown-red solution, without liberation of sulphurous acid; water throws down from the solution, after an hour, olive-green flocks, after twelve hours a violet precipitate; and the supernatant liquid, when evaporated and freed from sulphuric acid, yields easily soluble crystals (Stein).—4. When boiled with *dilute mineral acids*, rutin splits up into sugar (Stein) and quercetin (Hlasiwetz). The decomposition takes place with peculiar rapidity in an alcoholic solution; it is also effected by formic acid, especially at a temperature of, 110°. When rutin is dissolved in boiling acetic acid of 60 per cent., and again crystallised, the amount of carbon in the crystals (dried at 120°) is increased to 51·8 or 52 per cent.; it now reduces copper solutions, and has, therefore, been partly converted into quercetin (Stein). The decomposition is not effected by emulsin (Zwenger and Dronke). From 100 parts of rutin, dried at 100°, 39·24 to 43·25 parts (mean 41·9) of quercetin were obtained, corresponding with the equation,

$$C^{25}H^{28}O^{15} + 3H^2O = C^{13}H^{10}O^6 + 2C^6H^{12}O^6.$$

Calculation, 43·37 per cent. quercetin (Zwenger and Dronke). Hlasiwetz (Wien. Akad. Ber. 17, 400) obtained 58·03 per cent. quercetin and 44·5 per cent. sugar.

5. Rutin, treated in aqueous or alcoholic solution with *sodium-amalgam*, is converted into paracarthamin. (Stein, iv. 341.)

6. It reduces *nitrate of silver* and *trichloride of gold*, not cuprate of potassium. With water and *silver-oxide*, it forms a dark-red liquid, which leaves, on evaporation, a brown amorphous residue. (Stein.)

RUTINIC ACID. Syn. with Rutin.

RUTIN-SUGAR. This sugar, isomeric with glucose, is produced, together with quercetin, by boiling rutin with dilute sulphuric acid, and, after removing the quercetin and sulphuric acid, may be obtained, by evaporation, solution in alcohol, and precipitation with ether, as a colourless, uncrystallisable syrup. It does not act on polarised light; reduces cuprate of potassium in the cold; yields with boiling nitric acid, oxalic but no picric acid; and is not fermentable.

RUTYL. Syn. with *Capryl*, $C^{10}H^{19}O$, the radicle of rutic or capric acid. It is also applied, but incorrectly, to the alcohol-radicle $C^{10}H^{21}$, properly called *Decyl*. (See Appendix.)

RUTYLENE. $C^{10}H^{18}$. (A. Bauer, Ann. Ch. Pharm. cxxxv. 344; Bull. Soc. Chim. 1865, ii. 265.)—A hydrocarbon polymeric with acetylene, and perhaps identical with menthene, produced by the action of alcoholic potash on tribromide of diamylene, $C^{10}H^{20}Br^3$. It is related to diamylene and rutyl ($C^{10}H^{19}O$), in the same manner as valerylene, C^5H^8, is related to amylene and valeryl, and to campholic acid, $C^{10}H^{18}O^2$, in the same manner as crotonylene, C^4H^6, to crotonic acid, $C^4H^6O^2$.

Rutylene is a colourless liquid, lighter than water, and having an agreeable odour, somewhat like that of turpentine-oil. Boils at about 150°. Vapour-density, obs. = 4·843; calc. 4·778. It is insoluble in water, soluble in alcohol and in ether. Bromine attacks it strongly, with formation of hydrobromic acid and separation of charcoal. If, however, rise of temperature be prevented, dibromide of rutylene, $C^{10}H^{18}Br^2$, is formed. This is a very unstable compound, which decomposes even at ordinary temperatures, and acts strongly on acetate of silver and on alcoholic potash, probably forming, in both cases, the hydrocarbon $C^{10}H^{16}$.

RYACOLITE, or *Rhyacolite* (from ρύαξ, a lava-stream). A mineral from Vesuvius, having the crystallisation of felspar, and resembling the glassy variety. (Dana, ii. 245.)

RYE. See Cereals (i. 823).—Ergot of Rye (*Claviceps purpurea*. T.) contains, according to Neidhardt (N. Jahrb. Pharm. xviii. 193; Jahresb. 1862, p. 516), 31·06 per cent. fat oil, 2·69 resin, 1·3 red colouring matter, 0·8 mannite [mycose, according to Mitscherlich and Berthelot, iii. 1068], and 3·9 osmazome, together with phosphates, a volatile base (trimethylamine), gum, and fungin (cellulose with red colouring matter). The ergotine of Wiggers (ii. 499) is regarded by Neidhardt as resin.

Ergot may be detected in rye-flour by first boiling the flour twice with alcohol, to remove fatty and resinous matters, then treating the expressed residue with alcohol, and adding from 10 to 20 drops of dilute sulphuric acid. If the rye-flour is free from ergot, the liquid remains colourless, or exhibits only a faint yellowish tinge; in the contrary case, it acquires a red colour, more or less deep, according to the quantity of ergot present. (Jacoby, Anal. Zeitschr. iii. 509; Bull. Soc. Chim. 1866, i. 267. See also *Handwörterb. de Chem.* vii. 730.)

S.

SABADILLA SEEDS. The seeds of *Veratrum Sabadilla* (Retz), or *Veratrum officinale* (Schl.), a colchiaceous plant indigenous in Mexico, contain, according to Couerbe (Ann. Ch. Phys. [2] lii. 352), two organic bases, veratrine and sabadilline, and two acids, sabadillic or cevadic acid (i. 843), and veratric acid, together with helonin or veratrum-resin.

Sabadilline, $C^{20}H^{26}N^2O^5$, according to Couerbe, is extracted by exhausting the pulverised seeds with alcohol of specific gravity 0·845, treating the residue left on distilling off the alcohol with dilute sulphuric acid, decolorising the liquid with animal charcoal, and adding caustic potash, which precipitates sabadilline, hydrosabadilline, and veratrine, together with two non-basic substances. This precipitate is dissolved in dilute sulphuric acid, and the solution is mixed with nitric acid as long as a black pitchy precipitate is produced. The liquid filtered therefrom is precipitated by caustic potash; the precipitate is washed, dried, and dissolved in absolute alcohol; and the mass remaining after evaporation of the alcohol is boiled with water, which takes up sabadilline and hydrosabadilline. The former separates on cooling in stellate groups of apparently cubic crystals, which have a faint rose colour, but may be rendered colourless by recrystallisation.

Sabadilline has an extremely acrid taste: it begins to melt at 200°, and decomposes at higher temperatures, emitting fumes, and leaving a bulky cinder. It is moderately soluble in hot water, the solution having a distinct alkaline reaction, freely soluble in alcohol, insoluble in ether. It is decomposed by strong mineral acids, but forms crystallisable salts with dilute sulphuric and nitric acids.

According to Simon (Pogg. Ann. xliii. 493), sabadilline is not a definite substance, but a mixture of resin, alkali, and veratrine, the latter being precipitated by ammonia from the solution of the so-called sabadilline in sulphuric acid. According to Hübschmann, on the other hand (*Mittheilungen des Schweizer Apothekervereins*, Band iii. Heft 1), sabadilline is a definite compound, and is distinguished from veratrine by not exciting sneezing, by its insolubility in ether, and by not being precipitated by ammonia from its solution in sulphuric acid.

Hydrosabadilline or *Sabadilla gum-resin*, $C^{20}H^{28}N^2O^6$, differing from sabadilline by the elements of 1 at. water, is contained, according to Couerbe, in the aqueous mother-liquor of the latter, and separates on evaporation in oily drops, which solidify to a reddish resinous mass. It melts at 165°, is very soluble in alcohol, nearly insoluble in ether, has an alkaline reaction, and unites with acids, but does not form crystallisable salts.

SACCHARAMIDE. $C^6H^{12}O^6 = \left.\begin{matrix}H^4\\(C^6H^4O^2)^{vi}\\H^4\end{matrix}\right\}\begin{matrix}O^4\\N^2\end{matrix}$ (Heintz, Pogg. Ann. cvi. 93; Jahresb. 1859, p. 290.)—This compound separates as a white precipitate when dry ammonia-gas is passed into an ethereal solution of ethylic saccharate (p. 143). It may be crystallised from warm water, but is converted by boiling with water into saccharate of ammonium, and is quickly decomposed by acids into ammonia and saccharic acid.

SACCHARIC ACID. $C^6H^{10}O^8 = \left.\begin{matrix}H^4\\(C^6H^4O^2)^{vi}\\H^2\end{matrix}\right\}O^8$.— An acid, isomeric with mucic acid, produced by the action of nitric acid on cane-sugar, glucose, milk-sugar, and mannite. It was first observed by Scheele (*Opuscula*, ii. 203), who mistook it for malic acid, and it has been studied by Guërin-Varry (Ann. Ch. Phys. [2], xlix. 280; lii. 318; lxv. 332), Erdmann (Ann. Ch. Pharm. xxi. 1), Hess (*ibid.* xxvi. 1; xxx. 402), Thaulow (*ibid.* xxvii. 113), Liebig (*ibid.* xxx. 313; cxiii. 1; Jahresb. 1859, p. 261), and Heintz (Pogg. Ann. lxi. 315; cv. 211; cvi. 93; cxi. 265, 291; Jahresb. 1858, p. 251; 1859, p. 290; 1860, p. 259). See also Gm. xi. 513; Gerh. ii. 145: Kekulé's *Lehrbuch*, ii. 238.

Preparation.—1. One part of cane-sugar is warmed with 3 pts. nitric acid, of specific gravity 1·25 to 1·30, till a reaction is set up; the vessel is then removed from the fire; and after the first brisk action is over, and the liquid has cooled to 50°, it is kept at that temperature over a moderate fire as long as red fumes continue to escape. It is then diluted with half its bulk of water, and divided into two parts, one of which is saturated with carbonate of potassium, and then mixed with the other; or the entire liquid may be neutralised with the alkaline carbonate, and then treated with excess of acetic acid. The liquid, after several days' repose, deposits crystals of acid potassic saccharate, which may be purified by repeated crystallisation from boiling water, with addition of animal charcoal, if necessary (Heintz). Or the acid ammonium-salt may be prepared instead of the potassium-salt. (Liebig.)

2. When 1 pt. of milk-sugar is oxidised with 2½ pts. nitric acid of specific gravity 1·32, diluted with 2½ pts. water, mucic acid (about 33 per cent.) is first formed and separates out; and the liquid filtered therefrom, consisting chiefly of a solution of saccharic acid, may be concentrated at a gentle heat to about one-third, and neutralised with carbonate of potassium.

Free saccharic acid is best prepared from the cadmium-salt. The acid saccharate of potassium or ammonium is dissolved in boiling water; the solution, neutralised with potash or ammonia, is mixed at the boiling heat with the solution of a cadmic salt, and boiled for some time, and the cadmic saccharate thereby precipitated is decomposed by sulphydric acid. (Heintz.)

Properties.—Saccharic acid is not crystallisable, but if rise of temperature has been avoided during its preparation, it may be obtained in the form of a colourless brittle mass. It is deliquescent, easily soluble in *water* and *alcohol*, insoluble in ether. The solution of saccharic acid prepared from cane-sugar is dextrorotatory.

Decompositions.—Saccharic acid turns brown even at the heat of the water-bath. It reduces the metal from solution of *auric chloride*, and when heated, also from ammoniacal *silver-solution*. When oxidised by *nitric acid*, it yields, first, dextrotartaric, then oxalic acid. When heated with *hydrate of potassium* to 250°, it yields acetate and oxalate of potassium:

$$\underset{\text{Saccharate.}}{C^6H^8K^2O^8} + 2KHO = \underset{\text{Acetate.}}{2C^2H^3KO^2} + \underset{\text{Oxalate.}}{C^2K^2O^4} + 2H^2O.$$

Saccharates.—Saccharic acid is mostly dibasic, forming, with the alkali-metals, both neutral and acid salts. With lead, however, it forms a salt containing 3 at. of metal, which replace 6 at. of hydrogen.

The *acid potassium-salt*, $C^6H^9KO^8$, prepared as above, forms trimetric crystals, exhibiting the combination $\infty\bar{P}\infty\ .\ \infty P\ .\ \breve{P}\infty$. Angle $\infty P : \infty P = 103°26°$; $\bar{P}\infty : \breve{P}\infty = 131° 46$. Axes $a : b : c = 1{\cdot}7631 : 2{\cdot}2338 : 1$. Cleavage easy, parallel to oP. It is somewhat difficult of solution in water, 1 pt. of it requiring from 80 to 90 pts. of water. The *neutral potassium-salt*, $C^6H^8K^2O^8$, forms a crystalline crust. The *acid ammonium-salt*, $C^6H^9(NH^4)O^8$, forms quadrilateral prisms, about as soluble as the corresponding potassium-salt. The *neutral ammonium-salt* and the *sodium-salts* have not been obtained in the crystalline form.

Saccharate of barium, $C^6H^8Ba''O^8$, and the corresponding *strontium-* and *calcium-salts*, are precipitates insoluble in water, and when obtained from hot solutions, consist of microscopic crystals. Free saccharic acid does not precipitate the salts of barium, strontium, and calcium, but forms precipitates with baryta-, stontia-, and lime-water. Soluble saccharates, even the acid salts, form precipitates with barium-, strontium-, and calcium-salts.

The *magnesium-salt*, $C^6H^8Mg''O^8.3H^2O$, the *zinc-salt*, $C^6H^8Zn''O^8.H^2O$, and the *cadmium-salt*, $C^6H^8Cd''O^8$, are crystalline, nearly insoluble in cold water, somewhat soluble in boiling water. When neutral saccharate of potassium or ammonium is precipitated by a cold solution of cadmium-salt, a flocculent precipitate is formed, which cakes together into a resinous mass; if the two solutions are mixed at the boiling heat, a white heavy powder is formed, consisting of microscopic needles.

The *bismuth-salt* is obtained, as a flocculent precipitate, on adding neutral saccharate of potassium to a solution of bismuth-nitrate in a large quantity of water. The *copper-salt* is obtained by dissolving cupric hydrate in aqueous saccharic acid. The green solution, if free from excess of acid, deposits a green precipitate, which does not blacken when boiled. The *ferrous salt* is obtained, as a gummy mass, by dissolving metallic iron in saccharic acid and evaporating. *Ferric hydrate* dissolves with yellow colour in saccharic acid and saccharate of potassium.

Saccharates of Lead.—These salts vary greatly in composition, according to the manner in which they are prepared. When saccharate of potassium is boiled with excess of neutral lead-acetate, a resinous salt separates, agreeing approximately in composition with the formula $C^{12}H^{14}Pb''^3O^{16}$; and by boiling the solution decanted therefrom, an amorphous salt is obtained, corresponding with the formula $C^6H^6Pb''^2O^8$ (Heintz). Thaulow, by the same process, obtained a heavy granular precipitate, having nearly the composition $C^{12}H^{10}Pb''^5O^{16}$. If the boiling be prolonged, the precipitate becomes continually richer in lead, and after 9 or 10 hours' boiling, has the composition $C^6H^4Pb''^3O^8$. (Heintz.)

Saccharate of silver, $C^6H^8Ag^2O^8$, is obtained by mixing the neutral potassium-salt with nitrate of silver, as a white precipitate, which, in presence of an excess of the potassium-salt, remains white on boiling and becomes crystalline. It is very soluble in ammonia, the solution depositing metallic silver when boiled.

SACCHARIC ETHERS. *Neutral Ethylic saccharate*, $C^6H^8(C^2H^5)^2O^8$, is obtained by passing hydrochloric acid gas into a solution of saccharic acid in absolute alcohol; or, better, into absolute alcohol containing saccharate of calcium in suspension. In the latter case, a crystalline compound of ethylic saccharate and chloride of calcium, $2C^6H^8(C^2H^5)^2O^8.Ca''Cl^2$, separates, which is easily soluble in water, slightly soluble in alcohol, insoluble in ether. On dissolving this compound in a small quantity of water, adding a little alcohol, and a strong solution of sodic sulphate, evaporating quickly to dryness in a vacuum, exhausting the residue with alcohol, and adding a large quantity of ether, a solution is obtained, which, when left to evaporate, leaves the neutral ethylic saccharate in the form of a syrup, which gradually solidifies to a crystalline mass. It is easily soluble in water and in alcohol, slightly soluble in ether. The ethereal solution, treated with dry ammonia-gas, yields saccharamide (p. 142). (Heintz, Pogg. Ann. cv. 211; Jahresb. 1858, p. 251.)

Ethyl-saccharic acid, $C^6H^9(C^2H^5)O^8$, has not yet been obtained; but by passing hydrochloric acid gas into absolute alcohol in which acid saccharate of potassium was suspended, Heintz obtained a crystallisable compound, $C^6H^7(C^2H^5)O^8$, containing 1 at. water less than ethyl-saccharic acid—probably the ethylic ether of the first anhydride of saccharic acid: thus—

$$\underset{\text{Anhydride.}}{\left.\begin{matrix}(C^6H^4O^2)''\\ H^4\end{matrix}\right\}O^6} \qquad\qquad \underset{\text{Ether.}}{\left.\begin{matrix}(C^6H^4O^2)''\\ H^3(C^2H^5)\end{matrix}\right\}O^6}$$

SACCHARID. $C^6H^{10}O^5$.—A compound produced, according to Gélis (Compt. rend. xlviii. 1062; Jahresb. 1859, p. 547), by heating cane-sugar for some time to 160°. The sugar is then converted into a mixture of saccharid and dextroglucose: $C^{12}H^{22}O^{11} = C^6H^{10}O^5 + C^6H^{12}O^6$; it acquires the appearance of fruit-sugar; only half of it is fermentable; and it reduces only half as much cupric oxide in alkaline solution as an equal quantity of glucose or inverted sugar. By the action of dilute acids, however, it is rendered wholly fermentable, and then behaves towards reducing agents like ordinary glucose.

SACCHARIDES. Berthelot applies this term to compounds formed by heating dextroglucose, and other kinds of sugar, with organic acids. The formation of these compounds is attended with elimination of water, and they are capable of breaking up again, by assimilation of water, into the original acid and carbohydrate: *e.g.*—

$$\begin{array}{ccccccc}
2C^4H^8O^2 & + & C^6H^{12}O^6 & - & 3H^2O & = & C^{14}H^{22}O^7. \\
\text{Butyric acid.} & & \text{Glucose.} & & & & \text{Dibutyro-glucose.} \\
6C^2H^4O^2 & + & C^6H^{12}O^6 & - & 7H^2O & = & C^{18}H^{22}O^{11}. \\
\text{Acetic acid.} & & \text{Glucose.} & & & & \text{Hexaceto-glucose.} \\
4C^4H^6O^6 & + & C^6H^{12}O^6 & - & 5H^2O & = & C^{22}H^{26}O^{25}. \\
\text{Tartaric acid.} & & \text{Glucose.} & & & & \text{Glucoso-tetra-tartaric acid.}
\end{array}$$

The saccharides are subdivided into glucosides, or those produced from dextroglucose; levulosides, from lævo-glucose; galactosides, from lactose or milk-sugar; and inosides, from inosite. The naturally occurring bitter principles, which are resolvable by boiling with dilute acids into an organic acid and glucose, but have not been prepared artificially, are analogous in composition to Berthelot's saccharides. Berthelot likewise includes under *saccharides* the compounds formed by the action of acids on starch, dextrin, cellulose, and other carbohydrates: *e.g.*, xyloïdin from starch and nitric acid, pyroxylin from cellulose and nitric acid.

The formation of the saccharides occurs for the most part by long contact at 100° or 120°; with some kinds of sugar, as with trehalose, the temperature may be raised as high as 180°. Only a part of the sugar thus enters into combination.—They are decomposible into their constituents under the same conditions as the fats, but with greater difficulty. Water scarcely acts upon them at 100°; at higher temperatures the sugar itself would be destroyed. Continuous boiling with dilute acids decomposes them completely into the original acid and fermentable sugar; part of the latter, however, easily undergoes a further decomposition into glucic acid and humus-like bodies. Some saccharides suffer decomposition by contact with ferments.

The saccharides, like the natural fats, are soluble in water when they contain a volatile acid; insoluble when they contain a fixed acid. The soluble saccharides have an intensely bitter taste; they deflect the polarisation in the same direction as the sugar from which they are derived; none of them are volatile, but some of them emit a peculiar smell when warmed.

Respecting the classification of the saccharides, see Berthelot, *Chimie Organique fondée sur la Synthese*, ii. 271; also *Gmelin's Handbook*, xv. 317.

SACCHARIMETERS and **SACCHAROMETERS.** Instruments for determining the amount of sugar contained in solutions. The latter term is, however, applied more especially to hydrometers graduated for the purpose. (See SUGAR.)

SACCHARITE. A granular variety of andesin, having traces of cleavage in one direction, occurring in veins in serpentine at the chrysoprase mines near Frankenstein in Silesia. Specific gravity = 2·668. Contains, according to Schmidt (Pogg. Ann. lxi. 385), 58·93 per cent. silica, 23·50 alumina, 1·27 ferric oxide, 5·67 lime, 0·56 magnesia, 0·05 potash, 7·42 soda, 0·39 oxide of nickel, and 2·21 water.

SACCHAROID. A name given by Kane to a sweetish substance, probably identical with orcin, produced by the decomposition of Heeren's pseudo-erythrin (ethylic orsellinate).

SACCHAROMETER. See SACCHARIMETER.

SACCHARUM. Syn. with SUGAR.

SACCHULMIN, SACCHULMIC ACID. Brown substances obtained in the decomposition of sugar by dilute acids. (See ULMIN.)

SAFETY-LAMP. (See COMBUSTION, i. 1101.)

SAFETY-TUBE. An arrangement adapted to a gas-generating vessel, to prevent the liquid into which the delivery-tube dips, from passing back into the vessel, in consequence of diminished internal pressure. The simplest form consists of a straight tube passing through the cork of the generating vessel and dipping below the surface of the liquid, or of a tube bent twice at right angles, passing just through the cork, so that a portion of liquid may remain in the lower bend, and form a liquid joint, cutting off the communication between the inside of the vessel and the external air. In either case, when the pressure within the vessel becomes less than that of the atmosphere, air will pass in through the safety-tube and restore the equilibrium. The safety-tube likewise diminishes the danger of bursting from sudden increase of tension within the vessel. (For figures of various forms of safety-tube, see *Handwörterbuch der Chemie*, vii. 853.)

SAFFLORITE. Native arsenide of cobalt, containing a considerable quantity of iron. (See COBALT, i. 1042.)

SAFFLOWER. *Carthamus tinctorius* (i. 808).

SAFFRON. A yellow substance, consisting of the dried stigmas, with part of the styles, of the saffron crocus (*Crocus sativus*), a plant indigenous in Greece and Asia Minor, and extensively cultivated in Austria, France, and Spain, formerly also in England. The stigmas are from an inch to 1½ inch long, narrow and roundish where they are attached to the style, but spreading and club-shaped near the extremity, which is truncated. They have an orange or brownish-red colour, yellow in the narrower part, a strongly aromatic, almost intoxicating odour, an aromatic bitter taste, and impart a strong yellow colour to the saliva, as also to water, alcohol, and oils. Strong sulphuric acid colours them first indigo-blue, then red, and finally brown.

Saffron is used as a dye; also in medicine, chiefly for the colouring of tinctures, &c. On account of its high price, it is often adulterated with other substances of similar colour, such as the florets of the safflower or the marigold, slices of the flowers of the pomegranate, &c.; but these substances are easily detected, on close examination, by their different shape and colour. Saffron was formerly met with in two forms, called *hay-saffron* and *cake-saffron*; but the former is now alone in demand, the latter being entirely an artificial compound of the florets of the safflower, gum, and other materials.

According to an analysis by Bouillon-Lagrange and Vogel, saffron contains 7·5 per cent. of volatile oil (including stearoptene), 65·0 saffron-yellow or safranin, 0·5 wax, 6·5 gum, 0·5 albumin, 10·0 vegetable fibre, and 10·0 water.

Quadrat, by evaporating an ethereal extract of saffron, obtained a yellowish fatty body, which was partially soluble in boiling alcohol, and when treated with hot water left a snow-white residue, melting at about 48°. As the alcohol cooled, crystals separated out, while a fatty body (? oleic acid) remained in solution. Similar crystals were likewise obtained by directly boiling the saffron with absolute alcohol, and leaving the liquid to cool. Quadrat also found in saffron, glucose and a perhaps peculiar acid. Saffron when burnt left 8·9 per cent. ash, containing potash, soda, lime, magnesia, chlorine, sulphuric, phosphoric, silicic, and carbonic acids. (*Handw. d. Chem.*, vii. 51; *Penny Cyclopædia*, xx. 309.)

SAFRANIN, or **SAFFRON-YELLOW.** (Bouillon-Lagrange and Vogel, Ann. Chim. lviii. 198.—N. E. Henry, J. Pharm. viii. 399.—Quadrat, J. pr. Chem. lvi. 68.)—A colouring matter obtained, though not in the pure state, from saffron. Quadrat prepares safranin by first exhausting saffron with ether, then boiling it with water, and precipitating the decoction with acetate of lead, decomposing the precipitate with sulphydric acid, then washing it, and boiling it with alcohol of 40 per cent. The alcoholic solution when concentrated first deposits crystals of sulphur, and on evaporating the remaining liquid to dryness, dissolving in water, filtering, and again evaporating, safranin is obtained as a roseate inodorous powder, easily soluble with yellow colour in water and alcohol, very slightly soluble in ether, and slowly altering by exposure to light and air. It is coloured blue by strong sulphuric acid, green by nitric acid, blackish by hydrochloric acid. Rochleder (J. pr. Chem. lxxiv. 1) regards saffron-yellow as identical with the colouring matter of the pods of *Gardenia grandiflora*, and designates both as crocin (ii. 108).

SAGAPENUM. A gum-resin imported from Egypt and Persia, and probably derived from *Ferula persica*. It occurs in commerce, in yellow or reddish agglomerated granules, having an odour of garlic and an acrid bitter taste. It softens in the hand, but does not melt at a higher temperature. Contains, acording to Brandes, volatile oil, two resins, bassorin, gum, malic acid, ash, and impurities.—It yields umbelliferone by dry distillation (Sommer), and when treated with nitric acid, forms styphnic or other acids. (Böttger and Will; Brandes, N. Tr. ii. 2, 97; Pelletier, Bull. Pharm. iii. 481.)

The volatile oil of sagapenum is obtained by distillation with water. It is lighter than water, yellow, limpid, and has a repulsive odour of garlic. When exposed to the sun and air, the oil is converted into a transparent varnish, acquiring at the same time a smell of turpentine. Strong nitric acid, when heated with it, turns it thick and yellowish-red, with formation of oxalic acid. It assumes a dark-red colour with oil of vitriol, and dissolves in alcohol and ether. (Brandes.)

The alcoholic extract of sagapenum is resolved by ether into two resins:—*a*. The *resin insoluble in ether* is brown-yellow, brittle, inodorous and tasteless, and fusible when heated. It dissolves easily in warm caustic potash and in alcohol, but is insoluble in aqueous ammonia, and in volatile and fat oils.—*b*. The *resin soluble in ether* is red-yellow, transparent, tough at first, and has a slight odour of sagapenum, and a mild, afterwards bitter taste. It melts when warmed, and dissolves with dark-red colour in oil of vitriol. It dissolves slightly in aqueous ammonia, partially only in caustic potash, easily in alcohol and ether, and very slightly in hot oil of turpentine and oil of almonds. (Brandes.)

Sagapenum treated with cold alcohol of specific gravity 0·83, yields a pale-yellow solution, a considerable residue soluble in water remaining behind. The pale-yellow resin, which remains on evaporating the alcoholic solution, has a strong smell of garlic, melts at 100°, and gives up to water, when repeatedly boiled therewith, a substance having a bitter and onion-like taste: the residue dried at 110°, dissolved in alcohol, again evaporated, and dried at 66°, is semifluid, and contains 69·06 per cent. C, 8·51 H, and 21·43 O; after being melted for some hours at 100°, it is darker, but still remains sticky, and contains 69·84 per cent. C, 8·63 H, and 21·53 O. (Johnston, Phil. Trans. 1840, p. 361.)

SAGENITE. A variety of Rutile. (See TITANIUM.)

SAGO. A kind of starch, prepared in the islands of the Indian Archipelago, Madagascar, and Guinea, from the pith of the stems of certain palms: e.g., *Sagus Rumphii* W., *S. farinifera* Gärtn., *S. Raffia* Jacq., *S. Raphia* P. B., *S. lævis* Jacq., *S. genuina* Labill. &c.; and in China and Japan from certain Cycads, as *Cycas circinalis* L. and *Cycas revoluta* L. The pith is well stirred up with water on sieves; and the starch deposited from the water is washed, half dried in the air, then rubbed through suitable sieves, to granulate it; and finally dried, either in the open air, or in ovens at a heat of about 60°, whereby the grains become more or less horny and translucent.

Several kinds of sago are distinguished:—*White sago* forms irregular pure white grains; *red sago*, round regular grains, brown-red on one side; *brown sago*, round irregular grains of various sizes, and of a grey-brown colour, lighter in parts; *pearl sago*, yellowish grains of the size of a pin's head. The specific gravity of sago varies from 0·670 to 0·776. The grains, when steeped in cold water, take up more or less of it, and swell up to several times their original bulk, becoming transparent and gelatinous. The water takes up a small quantity of chloride of sodium, and gives a blue colour with iodine, as does also the swelled sago itself. The microscope shows that the external layers of the grains have been most disorganised by the heat employed in drying the sago.

The so-called "German sago" is prepared from ordinary wheat or potato-starch, and is granulated in the same manner as genuine sago. It is pure white, only partly semi-translucent, less hard and more friable than true sago.

SAHLITE. A variety of Augite, from Sahla, in Sweden. It has a dingy green colour, and is coarsely foliated, arising from composition parallel to the base.

SAL. The Latin names formerly used in chemistry to distinguish salts are in some cases still retained in pharmaceutical language. The following are examples of these names:—

Sal acetosellæ. Acid oxalate of potassium.
Sal alkali minerale. Carbonate of sodium.
Sal alkali vegetabile. Carbonate of potassium.
Sal alkali volatile siccum, or simply *Sal volatile*. Carbonate of ammonium.
Sal amarum. Sulphate of magnesium.
Sal aperitivum Fridericianum. Sulphate of sodium.
Sal auri philosophicum. Acid sulphate of potassium.
Sal catharticum. Sulphate of magnesium.
Sal cornu cervi. Carbonate of ammonium.

Sal de duobus. Neutral sulphate of potassium.
Sal digestivum Sylvii. } *Sal febrifugum Sylvii.* } Chloride of potassium.
Sal duplicatum. Neutral sulphate of potassium.
Sal martis. Crystallised ferrous sulphate.
Sal microcosmicum. Ammonio-sodic phosphate.
Sal mirabile perlatum. Disodic orthophosphate.
Sal narcoticum vitrioli. Boric acid.
Sal polychrestum Glaseri, S. Lamerianum, S. Parisiense. Neutral sulphate of potassium.
Sal polychrestum Seignetti. Tartrate of potassium and sodium.
Sal Saturni. Acetate of lead.
Sal secretum Glauberi. Sulphate of ammonium.
Sal sedativum Hombergii. Boric acid.
Sal succini. Amber.
Sal tartari. Carbonate of potassium.
Sal urinæ fixum, S. fusible, S. nativum. Ammonio-sodic phosphate.

SALAMANDER. The common salamander, *Lacerta salamandra* (L.), secretes, in the warts of its skin, a white milky liquid, which has a strong offensive odour and distinct acid reaction, is somewhat viscid when fresh, and quickly coagulates; alcohol causes it to coagulate immediately. This liquid, when introduced under the skin of other animals, exerts a strong poisonous action: in birds it produces violent convulsions, ending in death; in mammals the convulsions are much less violent, and the morbid symptoms ultimately disappear without fatal result. The poisonous principle is said to be of basic nature, and soluble in alcohol. (Gratiolet and Cloez, Compt. rend. xxxii. 592; xxxiv. 729.)

SALANGANA. *Hirundo esculenta.*—This bird is said to construct the edible nests obtained by the Chinese from the coasts of Cochin-China, Java, and other islands of the Indian Archipelago. According to Mulder (J. pr. Chem. xvii. 59), the nests usually have the form of a spoon without the handle; they are white or slightly coloured, have a vitreous fracture, and contain about 90 per cent. of a peculiar nitrogenous substance, which he calls *neossin*; also about 5 per cent. phosphates, and a small quantity of fat. According to Payen (*Précis de Chimie Industrielle*, 4me, éd. ii. 727), the nutritive matter of these nests, to which he gives the name of *cubilose*, exhibits the characters of the neutral albuminoïds.

SALEP. *Saleb, Salab.*—The tuberose roots of certain species of orchis, as *Orchis Morio, O. mascula, O. cariophorus, O. militaris, O. latifolia, O. maculata*, &c. The roots are gathered in summer, when the tuber of the previous year has died away, and the new one is fully developed. They are soaked for a few minutes in boiling water, and then dried. Salep thus prepared forms round or hand-shaped, somewhat flattened, horny, translucent, greyish-yellow lumps, having a sickly taste and faint peculiar odour, and easily reduced to a dirty yellow powder. In cold water this powder swells up slowly, in hot water quickly, to a bulky semi-transparent jelly. One pt. of salep is capable of converting 48 pts. of boiling water into a thick gum, which becomes compact and solid on the addition of magnesia or of borax.

According to some authorities, salep consists chiefly of a gum resembling bassorin (ii. 955), with small quantities of starch and gum; according to Mulder (Ann. Ch. Pharm. xxvii. 283), of pectic acid. According to Schmidt (*ibid.* li. 29), salep, when examined with the microscope, exhibits distinct grains of starch, or at all events of a substance which is turned blue by iodine. Salep-mucilage liquefies when digested with dilute sulphuric acid, the amylaceous substance being converted into gum and sugar, while the cellular membrane forms a precipitate. Salep-bassorin appears to consist merely of this membrane swollen by water. Pulverised salep, dried at 100°, left 1·59 per cent. ash, consisting of calcic carbonate with calcic and magnesic phosphates.

SALHYDRAMIDE. Syn. with HYDROSALICYLAMIDE (iii. 218).

SALICIN. $C^{13}H^{18}O^7$.—(Leroux, Ann. Ch. Phys. [2] xliii. 440.—Braconnot, *ibid.* xliv. 296.—Pelouze and Gay-Lassac, *ibid.* xliv. 220; xlviii. 111.—Piria, *ibid.* lxix. 281; [3] xiv. 257.—Bouchardat, Compt. rend. xviii. 299; xix. 602; xx. 610, 1635.—Gerhardt, Ann. Ch. Phys. [3] vii. 215; *Traité*, iii. 311.—Gm. xv. 430.)—This substance, discovered by Leroux, an apothecary of Vitry-le-Français, exists ready-formed in the barks of several species of willow and poplar, especially, according to Braconnot, in that of *Salix helix, S. amygdalina, Populus tremula*, and *P. græca.* It appears also to be contained in the flower-buds of meadow-sweet (*Spiræa Ulmaria*), and in the green parts of this and other herbaceous spiræas, inasmuch as these plants yield salicylol by distillation with water (Buchner, N. Repert. Pharm. ii. 1); also in castoreum (i. 814), being derived from the willow-barks which constitute the principal food of the beaver. (Wöhler.)

Salicin is produced artificially:—1. By the action of nascent hydrogen on helicin, $C^{13}H^{16}O^7$ (iii. 139). When an aqueous solution of that substance is digested with sodium-amalgam, and evaporated to dryness after supersaturation with carbonic acid, salicin remains in the residue, and may be extracted therefrom by alcohol (**Lisenko.** Zeitschr. Ch. Pharm. 1864. p. 577).—2. Together with benzoic acid, by boiling populin (iv. 690) with lime- or baryta-water:

$$\underset{\text{Populin.}}{C^{20}H^{22}O^{8}} + H^{2}O = \underset{\text{Benzoic acid.}}{C^{7}H^{6}O^{2}} + \underset{\text{Salicin.}}{C^{13}H^{18}O^{7}}.$$

Or, together with ethylic benzoate and benzamide, by heating populin to 100° in a sealed tube with alcoholic ammonia. (**Piria**).

Preparation.—1. Six pounds of dry chopped willow or poplar bark are boiled with water; the liquid is strained, concentrated down to 18 pounds, mixed while still hot with 2 pounds of levigated oxide of lead, digested for 24 hours, and again strained; the residue is thoroughly washed; and the filtrate is evaporated to a syrup, and left to crystallise. An additional quantity of salicin is obtained from the mother-liquors after they have again been treated with oxide of lead, and the entire product is purified by repeated crystallisation (**Duflos**, Schw. J. lxvii. 25).—2. The aqueous decoction of the bark is precipitated with basic acetate of lead; the filtrate is boiled with chalk, till the excess of the basic acetate is decomposed, and the liquid becomes clear and colourless; then evaporated to an extract; and this extract is exhausted with alcohol of 34°, and left to crystallise (**Peschier**, Ann. Ch. Phys. [2] xliv. 418).—3. Sixteen pts. of bark are macerated with 2 pts. lime and with water for 24 hours; the mixture is boiled for half an hour, and strained; the residue is treated in like manner with the same quantity of lime as before; and the whole of the liquids are decanted from the sediment, concentrated, then mixed with 6 to 8 pts. of bone-black, and evaporated to complete dryness. The residue, after being pulverised, is exhausted at a gentle heat with alcohol of 82 per cent., and the alcohol is distilled off from the tinctures; the salicin then crystallises from the residue in pale-yellow granules, which are purified by recrystallisation with help of animal charcoal. (**Erdmann**, Berl. Jahrb. xxxiii. 1, 136.)

Properties.—Salicin crystallises in broad, tabular, or mostly scaly crystals, belonging to the trimetric system, and exhibiting the combination $\infty P . \infty\breve{P}\infty . \breve{P}\infty$. Axes, $a:b:c$, = 0·9274 : 2·4938 : 1. Angle, $\infty P : \infty P = 139° 12'$, $\breve{P}\infty : \breve{P}\infty = 136° 18'$ (**Schabus**). It is white, soluble in water and in alcohol, insoluble in ether and in oil of turpentine. Water at ordinary temperatures dissolves about 5 pts. of salicin; alcohol much less. It melts at 120°, does not give off water till heated to 200°, and decomposes at a higher temperature. Its solutions have a bitter taste, and do not alter vegetable colours. According to some authorities, it possesses febrifugal properties. The solutions turn the plane of polarisation of light to the left; $[\alpha]r = -55·8°$.

Salicin is not precipitated by neutral or basic acetate of lead, by gelatin, or by infusion of galls.

According to **Phipson** (*Chem. News*, vi. 278), an alcoholic solution of 1 at. salicin and 1 at. benzoic acid yields crystals of populin. Salicin also forms crystallisable compounds with tartaric and citric acids. According to **O. Schmidt** (Bull. Soc. Chim. 1866, i. 287) salicin does not yield populin when heated as just mentioned: heated in a sealed tube with benzoic acid and water, it yields a yellow resinous body (saliretin?) and a solution which colours ferric chloride blue (saligenin?).

Decompositions.—1. Salicin heated to 260° gives off water and salicylous acid, together with acid vapours having an odour of caramel, and leaves a yellow residue insoluble in water, which turns brown, and ultimately carbonises. By dry distillation it yields salicylol, together with aromatic products. When distilled with *soda-lime*, it yields a mixture of phenol and salicylol (**Gerhardt**).—2. By the current of a Bunsen's battery of 400 pairs, salicin is resolved into glucose and saligenin, which latter is then converted into salicylol, and ultimately into salicylic acid (**Tichanowitsch**, Petersb. Acad. Bull. iv. 80).—3. It is not altered by *ozone*. (**Gorup-Besanez**, Ann. Ch. Pharm. cx. 106.)

4. When boiled with water and *peroxide of lead*, it yields a solution of lead-formate, and a lead-compound of salicin. Distilled with *peroxide of manganese* and dilute sulphuric acid, it yields large quantities of formic acid and carbonic anhydride; but a mixture of sulphuric acid and *dichromate of potassium* converts it into carbonic anhydride, formic acid, and salicylol.

5. Salicin is coloured red by strong *sulphuric acid*, and the product is decolorised by water; the solution then contains a conjugated acid (**Mulder's** *sulphorufic acid*), together with unaltered salicin. If the mixture be heated, there is also formed a resinous substance, called **olivin** by Mulder, **rutilin** by Braconnot, and probably identical with Piria's **saliretin** (*q. v.*). The red colour imparted to salicin by strong sulphuric acid may serve for the detection of salicin in willow-bark.

6. Salicin heated with *dilute sulphuric* or *hydrochloric acid* is resolved into glucose and saligenin:

$$C^{13}H^{18}O^7 + H^2O = C^6H^{12}O^6 + C^7H^8O^2.$$

The same transformation is effected by contact with water and *emulsin*, at a temperature not above 40° (Piria); or by digestion with *saliva* at 38° or 40°. (Städeler, J. pr. Chem. lxxii. 350.)

7. Salicin treated with very weak *nitric acid*, at ordinary temperatures, is converted into helicin:

$$C^{13}H^{18}O^7 + O = C^{13}H^{16}O^7 + H^2O.$$

Sometimes helicoïdin is formed instead of helicin, especially if the acid has a density of about 12° Bm. (Piria). When salicin is boiled once or twice with nitric acid diluted with ten times its bulk of water, it turns yellow and gives off red vapours, together with the odour of salicylol; and the solution, if then mixed with a ferric salt, acquires the colour of ink. The same solution, when left at rest, deposits salicylous acid, the quantity of which gradually increases on evaporation at a gentle heat, without boiling. But if the liquid be again boiled, it becomes clear, and then on cooling deposits, after a while, needles of nitrosalicylic acid, which are reddened by ferric salts (Gerhardt). By the prolonged action of nitric acid, the salicin is ultimately converted into picric acid, together with oxalic acid. (Braconnot.)

8. Salicin added by small portions to boiling aqueous caustic *soda*, dissolves with effervescence, and the solution when saturated with an acid deposits saliretin. On distilling the neutralised solution, salicylol passes over, and a residue is left containing salicylic acid and a brick-red powder (Bouchardat, Compt. rend. xix. 1179).—9. Fused with excess of *potash*, it gives off a large quantity of hydrogen, and is ultimately converted into salicylate and oxalate of potassium.

10. *Chlorine* converts salicin into chlorosalicin, dichlorosalicin, and perchlorosalicin.—11. A mixture of *hydrochloric acid* and *chlorate of potassium* transforms it into perchloroquinone (p. 29). Salicin distilled with *hypochlorite of calcium* yields chloropicrin, but no perchloroquinone (Stenhouse, Ann. Ch. Pharm. lv. 4; lxvi. 247).—12. An aqueous solution of salicin mixed with *chloride of iodine* solidifies, after a while, to a white magma of crystals containing iodine, which have not been further examined. (Stenhouse, Chem. Soc. J. xvii. 327.)

13. After the ingestion of salicin into the animal body, salicylol and salicylic acid are found in the urine (Laveran and Millon, Ann. Ch. Phys. [3] xiii 145). If the dose is large, the urine contains also unaltered salicin, together with saligenin, and perhaps also phenol. (Ranke, J. pr. Chem. lvi. 1.)

Substitution-derivatives of Salicin.

Benzosalicin. $C^{20}H^{22}O^8 = C^{13}H^{17}(C^7H^5O)O^7$.—This is the composition of *Populin*, a crystallisable substance obtained from the bark, leaves, and root of the aspen (iv. 689).

Chlorosalicin. $C^{13}H^{17}ClO^7$. (Piria, [3] xiv. 275.)—Crystallised salicin exposed to the action of chlorine gas, is converted into a red resinous substance, with copious evolution of hydrochloric acid; but when chlorine is passed into a pulp composed of 1 pt. of finely pulverised salicin and about 4 pts. of water, the whole gradually dissolves, and chlorosalicin separates as a nacreous crystalline precipitate, which must be pressed in a cloth, dried between bibulous paper, shaken up two or three times with ether to remove adhering resinous matter, and crystallised from boiling water.

Chlorosalicin crystallises in long, very light, silky needles containing $C^{13}H^{17}ClO^7.2H^2O$. It is soluble in water and alcohol, insoluble in ether. When heated, it first gives off its water, then melts to a transparent colourless liquid, and finally decomposes, giving off vapours of hydrochloric acid, and leaving a large quantity of charcoal. In contact with emulsin it is quickly resolved into glucose and chlorosaligenin, $C^{14}H^7ClO^2$. Strong sulphuric acid dissolves it with reddish colour. When heated with dilute acids, it is quickly resolved into glucose, and a resin resulting from the metamorphosis of chlorosaligenin. (Piria.)

Dichlorosalicin, $C^{13}H^{16}Cl^2O^7$, is obtained by the action of chlorine on the preceding compound, or by its prolonged action on salicin. It forms long, silky, snow-white needles, containing 2 at. water, which they give off at 100°. It is inodorous, slightly bitter, nearly insoluble in cold water, sparingly soluble in boiling water, moderately soluble in alcohol, and nearly insoluble in ether. By dry distillation it yields chlorosalicylol, together with other products. Its aqueous solution does not precipitate metallic salts. Dilute acids convert it into glucose and a reddish resin. Emulsin acts upon it in the same manner as on monochlorosalicin. (Piria.)

Perchlorosalicin, $C^{13}H^{15}Cl^3O^7$, is formed when chlorine is passed into a heated mixture of water and dichlorosalicin, containing lumps of marble to neutralise the hydrochloric acid as fast as it is formed. It is then precipitated as a yellow crystalline powder, which must be shaken two or three times with ether, and crystallised from weak alcohol. It forms small yellowish needles, containing 2 at. water, which is given off at 100°. It is inodorous, but has a bitter taste, decomposes when heated above 100°, and is resolved by emulsin into glucose and a resinous product. (Piria.)

Plumbosalicin, $C^{13}H^{14}Pb^2O^7$ [?], is obtained by pouring a few drops of ammonia into a hot strong solution of salicin, and gradually adding basic acetate of lead till about half the salicin is precipitated. The lead-compound then separates as a bulky white precipitate, resembling starch when dried, having a bitter and sweetish taste, soluble in acetic acid and in potash. It does not give off any water at 100°. It is decomposed by the weakest acids, salicin being set free. Strong sulphuric acid colours it red.

Lead-compounds of salicin of different composition are obtained under other circumstances, not very well defined. (Piria.)

SALICOSYL. $C^7H^5O^2$. A monatomic radicle which may be supposed to exist in salicylol, or salicylous hydride, $C^7H^5O^2.H$, and its derivatives (p. 161). It was formerly called *salicyl*, but this name belongs properly to the diatomic radicle of salicylic acid.

SALICYL. C^7H^4O. The diatomic radicle of salicylic acid and its derivatives. Not known in the separate state.

SALICYL-ACETIC ACID. $C^9H^8O^4 = \left.\begin{matrix}(C^7H^4O)''\\C^2H^3O\\H\end{matrix}\right\}O^2$.—*Acetosalicylic acid.*

[Formerly regarded as *Acetosalicylic anhydride*, $C^7H^5O^2.C^2H^3O$, in accordance with the monatomic formula of salicylic acid, $C^7H^5O^2.H.O$]. Discovered by Gerhardt, who obtained it by the action of chloride of acetyl on salicylate of sodium (i. 31). It is also produced by heating salicylic acid with chloride of acetyl. As thus obtained, it crystallises in tufts of slender prisms, dissolves completely in water only at the boiling heat, easily in alcohol and ether, and reacts with ferric salts like salicylic acid. It melts easily, and when heated a little above its melting-point, emits the odour of acetic acid. It dissolves in warm nitric acid of specific gravity 1·2, the solution yielding crystals of a nitro-acid. (H. v. Gilm, Ann. Ch. Pharm. cxii. 180.)

SALICYLAMIC ACID. $C^7H^7NO^2 = \left.\begin{matrix}H^2\\(C^7H^4O)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (Cahours, Ann. Ch. Phys. [3] x. 349.—Muspratt and Hofmann, Ann. Ch. Pharm. liii. 226.—Limpricht, *ibid.* xcviii. 256; xcix. 249.)—This compound, metameric with oxybenzamic acid, phenyl-carbamic acid, and nitrotoluene, and formerly regarded as *salicylamide*, $N.H^2.C^7H^5O^2$ (that is, as the amide of monobasic salicylic acid, $C^7H^5O^2.H.O$), is produced by the action of ammonia on methylsalicylic or ethylsalicylic acid:

$$\underset{\substack{\text{Methylsalicylic}\\\text{acid.}}}{C^7H^5(CH^3)O^3} + NH^3 = \underset{\substack{\text{Salicylamic}\\\text{acid.}}}{C^7H^7NO^2} + \underset{\substack{\text{Methyl-}\\\text{alcohol.}}}{CH^4O}.$$

To prepare it, 1 vol. of wintergreen-oil (methylsalicylic acid) is mixed and repeatedly agitated with about 6 vols. of strong alcoholic ammonia. The yellowish-brown solution thus obtained, deposits, on evaporation, needles of salicylamic acid, which may be purified by crystallisation from hot water or alcohol.

According to Cahours, it is produced by heating acid salicylate of ammonium, but Limpricht was not able to prepare it in this way.

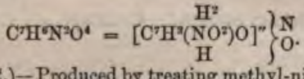
Salicylamic acid crystallises in laminæ having a strong lustre, and a yellowish-white colour not removable by treatment with animal charcoal. It has an acid reaction, is nearly insoluble in cold water, easily soluble in hot water, also in alcohol and in ether. It melts at 132°, and boils at 270°, giving off an aromatic vapour which condenses to shining laminæ of the acid. If it be kept at this temperature till about a fourth part has volatilised, the residue contains salicylimide, which may be extracted by alcohol:

$$C^7H^7NO^2 - H^2O = C^7H^5NO.$$

This reaction affords a decided proof of the diatomicity of salicylic acid, since monatomic acids do not form amic acids and imides (i. 47, 171). Salicylamic acid passed over red-hot lime, is resolved into ammonia, aniline, and phenol. With fuming nitric acid, it forms a nitro-substitute. Strong acids and alkalis convert it, by assumption of water, into acid salicylate of ammonium, $(C^7H^4O)''(NH^4).H.O^2$.

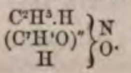
Salicylamates.--Salicylamic acid is so weak an acid, that it is not capable of uniting directly with ammonia, or decomposing alkaline carbonates, but crystallises unaltered from the solution, on evaporation.—The *barium-salt*, $C^{14}H^{12}Ba''N^2O^4$ (at 100°), is soluble in water, and is obtained by treating the acid with baryta-water in a vessel protected from the air.—The *strontium-, calcium-, and magnesium-salts* are similar in properties and composition, and are obtained in like manner; the last, by adding the acid to magnesia suspended in water. All these salts are decomposed by carbonic acid.—The *potassium-* and *sodium-salts* are obtained, as radio-crystalline masses, by decomposing the barium-salt with the corresponding sulphates, and evaporating the filtrate.—*Cupric salicylamate*, $C^{14}H^{12}Cu''N^2O^4$, is precipitated in bright-green microscopic needles, on adding cupric acetate to a solution of either of the preceding salts.—The *silver-salt*, $C^7H^6AgNO^2$ (dried over oil of vitriol) is a greyish-white, not perceptibly crystalline precipitate, which blackens on boiling the liquid. (Limpricht.)

Substitution-derivatives of Salicylamic Acid.



Nitrosalicylamic acid. $C^7H^6N^2O^4 = \left.\begin{matrix} H^2 \\ [C^7H^3(NO^2)O]'' \\ H \end{matrix}\right\} \begin{matrix} N \\ O. \end{matrix}$ *Nitrosalicylamide, Anilamide.* (Cahours, *loc. cit.*)—Produced by treating methyl-nitrosalicylic acid with ammonia in the manner above described: its preparation takes, however, a much longer time (two or three weeks) than that of salicylamic acid, because methyl-nitrosalicylic acid dissolves but slowly in alcoholic ammonia.

Nitrosalicylamic acid is soluble in hot water, alcohol, and ether, and when recrystallised from alcohol, forms yellow needles, which sublime when cautiously heated. It dissolves easily in alkalis, and is precipitated unaltered by acids. The aqueous solution colours ferric salts red. When heated with strong acids or alkalis, it is resolved into ammonia and nitrosalicylic acid. Its salts are not known.

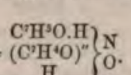


Ethylsalicylamic acid, $C^9H^{11}NO^2 = \left.\begin{matrix} C^2H^5.H \\ (C^7H^4O)'' \\ H \end{matrix}\right\} \begin{matrix} N \\ O. \end{matrix}$ (Limpricht, Ann. Ch. Pharm. xcviii. 262.)—Produced by the action of aqueous ammonia on ethylic methyl-salicylate:

$$C^7H^4(CH^3)(C^2H^5)O^3 + NH^3 = C^7H^6(C^2H^5)NO^2 + CH^4O.$$

If the materials are left to act in the cold, colourless needles of ethylsalicylamic acid are obtained in a few days; if they are heated to 100° in a sealed tube, the action is complete in a few hours.

Ethylsalicylamic acid is soluble in hot water, in alcohol, and in ether, and separates from the ethereal solution in crystals of considerable size. It melts at 110° in the dry state, at 100° when heated with water, and solidifies to a crystalline mass, which sublimes at a stronger heat. From solution in warm potash-ley, hydrochloric acid, or nitric acid, it separates unaltered on cooling; from solution in sulphuric acid on dilution with water. The aqueous solution has a slight acid reaction. It is coloured red by ferric chloride, green by cupric sulphate, and is precipitated by ammoniacal acetate of lead.



Benzoylsalicylamic acid, $C^{14}H^{11}NO^3 = \left.\begin{matrix} C^7H^5O.H \\ (C^7H^4O)'' \\ H \end{matrix}\right\} \begin{matrix} N \\ O. \end{matrix}$ *Benzoylsalicylamide. Salicylbenzamide.* (Gerhardt and Chiozza, Compt. rend. xxxvii. 86.—Limpricht, Ann. Ch. Pharm. xcix. 249.)—Produced by the action of salicylamic acid on chloride of benzoyl. A mixture of the two substances in equivalent quantities is heated to 120°—145° as long as hydrochloric acid continues to escape; and the residue, which remains liquid and viscid for a long time after cooling, but becomes crystalline on the addition of a few drops of alcohol or ether, is washed with a small quantity of ether and dissolved in boiling alcohol, whence it crystallises on cooling in very slender needles united in flocks.

The acid when heated gives off 1 at. water, and is converted into benzoylsalicylamide, $C^{14}H^9NO^2$ (Limpricht). It dissolves very easily in ammonia, but is deposited in its original state when the ammonia evaporates, or when the solution is mixed with an acid; also in the fixed alkalis, forming deep yellow solutions, but is generally resolved at the same time into benzoic and salicylamic acids (Limpricht). It dissolves in warm carbonate of sodium without evolution of carbonic anhydride, and the solution, when treated with acids, deposits very soluble crystals, probably consisting of benzoic and salicylamic acids (Limpricht). Its solution in strontia-water first deposits crystals of benzoate, and afterwards of salicylamate of strontium.

The ammoniacal solution forms a light lemon-yellow precipitate with neutral acetate of lead, and light-blue with sulphate of copper. (Gerhardt and Chiozza.)

Silver-salt.—The ammoniacal solution of the acid forms with nitrate of silver a light lemon-yellow precipitate, which becomes strongly heated with chloride of benzoyl, forming chloride of silver. (Gerhardt and Chiozza.)

Cumylsalicylamic acid, $C^{17}H^{17}NO^2 = \left.\begin{matrix}C^{10}H^{11}O.H\\(C^7H^4O)''\\H\end{matrix}\right\}\begin{matrix}N\\O.\end{matrix}$ —Prepared, like the preceding, with salicylamic acid and chloride of cumyl. Crystallises from alcohol in capillary needles. (Gerhardt and Chiozza.)

SALICYLAMIDE, $C^7H^8N^2O = \left.\begin{matrix}(C^7H^4O)''\\H^4\end{matrix}\right\}N^2$, appears to be produced by the prolonged action of ammonia on ethylic methylsalicylate. (Limpricht, Ann. Ch. Pharm. xcviii. 262.)

SALICYLBENZOIC ACID. $C^{14}H^{10}O^4 = \left.\begin{matrix}(C^7H^4O)''\\C^7H^5O\\H\end{matrix}\right\}O^2$. Syn. with BENZOSALICYLIC ACID (i. 565).

SALICYLIC ACID. $C^7H^6O^3 = \left.\begin{matrix}(C^7H^4O)''\\H^2\end{matrix}\right\}O^2$. *Spinoylic acid. Hyperspiroylic acid.* (Piria, Ann. Ch. Pharm. xxx. 165; xciii. 262.—Löwig and Weidmann, J. pr. Chem. xix. 236; Pogg. Ann. xlvi. 83.—Marchand, J. pr. Chem. xxvi. 395.—Procter, J. Pharm. [3] iii. 275.—Delalande, Ann. Ch. Phys. [3] vi. 346.—Gerhardt, *ibid.* vii. 217.—Cahours, *ibid.* x. 327; xiii. 90, 113.—Ettling, Ann. Ch. Pharm. liii. 77.—Schlieper, *ibid.* lix. 26.—Kolbe and Lautemann, Ann. Ch. Pharm. cxiii. 125; cxv. 157; cxx. 299; Jahresb. 1859, p. 309; 1860, p. 287; 1861, p. 393.—Kekulé, Ann. Ch. Pharm. cxvii. 145; Jahresb. 1860, p. 293.—Gm. xii. 246.—Gerh. iii. 320; iv. 1017.)

This acid, metameric with oxybenzoic acid, exists ready-formed in the flowers of *Spiræa Ulmaria*, and as methylsalicylic acid in oil of wintergreen.

Formation.—1. From salicylol by oxidation wiith aqueous chromic acid (Ettling), or by heating with oxide of copper (Ettling, Piria).—2. By melting salicylol or salicin with hydrate of potassium (Piria):

$$\underset{\text{Salicylol.}}{C^7H^6O^2} + KHO = \underset{\substack{\text{Potassic}\\\text{Salicylate.}}}{C^7H^5KO^3} + H^2.$$

—3. By heating indigo with hydrate of potassium to 300°. The experiment does not always succeed: if the heat be not continued long enough, only phenyl-carbamic acid is produced; if too long, a brown substance is formed. (Ettling.)

5. By passing carbonic anhydride into phenol containing small pieces of sodium. The metal then dissolves with evolution of hydrogen, and salicylate of sodium is formed, together with other products. Salicylic acid has, in fact, the same composition as phenyl-carbonic acid: $C^6H^6O + CO^2 = C^7H^6O^3$ (Kolbe and Lautemann).—6. By the action of nitrous acid on phenyl-carbamic acid (Gerland):

$$C^7H^7NO^2 + HNO^2 = C^7H^6O^3 + H^2O + N^2.$$

Griess (Jahresb. 1861, p. 413), by the action of nitrous acid on phenyl-carbamic acid, obtained an acid, which he calls diazo-salyl-nitric acid, having the composition $C^{14}H^9N^3O^7$; and this, when heated in an aqueous solution, is completely resolved into salicylic acid, nitric acid, and free nitrogen:

$$C^{14}H^9N^3O^7 + 2H^2O = 2C^7H^6O^3 + NHO^3 + N^2.$$

7. Coumaric acid (ii. 93), heated with hydrate of potassium, yields salicylate and acetate of potassium (Delalande, Ann. Ch. Phys. [3] vi. 343):

$$C^9H^8O^3 + 2KHO = C^7H^5KO^3 + C^2H^3KO^2 + H^2.$$

8. Methylsalicylic acid (oil of wintergreen) is resolved by gaseous hydriodic acid into salicylic acid and methylic iodide (Lautemann, Ann. Ch. Pharm. cxxv. 13):

$$C^7H^5(CH^3)O^3 + HI = C^7H^6O^3 + CH^3I.$$

9. Iodosalicylic acid is decomposed by hydriodic acid, even at temperatures below 100°, and more quickly at 100°, into salicylic acid and free iodine (Kekulé, Chem. Soc. J. xvii. 203):

$$C^7H^5IO^3 + HI = C^7H^6O^3 + I^2.$$

Preparation.—*a.* From the flowers of *Spiræa Ulmaria.* The flowers are exhausted with ether, or the water distilled from them, with frequent cohobation, is shaken up with ether; the ethereal solution is distilled; the residue is treated with water, which dissolves salicylic acid and tannin; and the aqueous solution is neutralised with carbonate of potassium, evaporated, and distilled with hydrochloric acid. The watery distillate slowly evaporated yields colourless needles. (Löwig and Weidmann.)

b. From *Oil of Gaultheria* (*Wintergreen*).—The oil is heated with strong potash-ley till no more methylic alcohol is given off from it, and the residue is precipitated with hydrochloric acid. The precipitate is washed with cold water, and crystallised from hot alcohol. (Cahours.)

c. From *Salicylol*, or from *Salicin*.—1. Hydrate of potassium is heated in a silver basin, and as soon as it is melted, salicin is added by small portions, with continual stirring; whereupon the mass turns brown, swells up, and gives off a large quantity of hydrogen. It is then heated as long as hydrogen is given off in presence of excess of potash. If the potash is not in excess, only a small quantity of salicylic acid is obtained, but instead of it, salicylol and a brown resinous substance which it is difficult to convert into salicylic acid, even by repeated fusion with hydrate of potassium. If the process be rightly conducted, the mass becomes nearly colourless, exhibiting only a slight yellowish tint. The mass is dissolved in water; the solution is supersaturated with hydrochloric acid, the vessel being surrounded with cold water; and the resulting crystalline mass is separated from the mother-liquor (which contains oxalic acid), and recrystallised from hot water (Piria, Gerhardt, Marchand).—2. Cupric salicylate is heated in a retort till nothing more escapes at 220°, and the residue has assumed a uniform kermes-brown tint. This residue, consisting of cuprous salicylite, is then introduced into a glass tube, and sulphuretted hydrogen passed over it, whereupon the mass becomes heated and blackened, and salicylic acid sublimes; and in order that the sublimate may not cover up the undecomposed mass, and so protect it from further decomposition, it must be driven forward by the application of a gentle heat. Or the cuprous salicylate is dissolved in warm acetic acid, or in hydrochloric acid diluted with an equal quantity of water; the colourless liquid is precipitated by sulphuretted hydrogen, and the liquid filtered from the sulphide of copper is evaporated to the crystallising point. Or the solution of the copper-salt in acetic acid is supersaturated with ammonia, and precipitated with neutral acetate of lead, the precipitate suspended in hot water, sulphuretted hydrogen passed through the liquid, and the sulphide of lead removed by filtration: the filtrate on cooling yields pure salicylic acid. (Ettling.)

d. From *Indigo* (p. 152).—The heat must be carefully regulated, because, if the required temperature is exceeded, the salicylic acid decomposes, and a brown substance is formed; and if the heating is not continued long enough, nothing but phenyl-carbamic acid is produced.

e. From *Phenol*.—Dry carbonic anhydride is passed into warm phenol, with addition of small pieces of sodium. The metal then dissolves with evolution of hydrogen, and a stiff paste is formed, containing the isomeric salts, salicylate and phenyl-carbonate of sodium, together with unaltered phenol. On acidulating with hydrochloric acid, the phenyl-carbonic acid is decomposed with evolution of carbonic anhydride, and the salicylic acid which is set free may be separated from the phenol by solution in strong aqueous carbonate of ammonium. The solution boiled down till it acquires a slight acid reaction, filtered from separated resin, and mixed with hydrochloric acid, yields salicylic acid, to be purified by recrystallisation with aid of animal charcoal. Salicylic acid is also formed, though in much smaller quantity, by passing carbonic anhydride into a ready-prepared solution of phenylate of sodium in phenol. (Kolbe and Lautemann, Ann. Ch. Pharm. cxv. 177.)

Properties.—Salicylic acid crystallises by spontaneous evaporation of its alcoholic solution in large monoclinic four-sided prisms. From a hot aqueous solution it separates on cooling, in slender needles often an inch long. Particularly large and fine crystals are obtained by slow evaporation of the ethereal solution (Cahours). It melts at 158° (Cahours), at 121° (Procter), at 125° (Ettling). Sublimes at about 200°, without boiling, in slender needles having a strong lustre, and, when pure, may be completely distilled by careful heating (Cahours, Ettling). It has a sweetish-sour taste, and produces irritation in the throat. Reddens litmus rather strongly. It does not act on polarised light.

It is slightly soluble in cold, much more soluble in hot *water*; still more in *alcohol*, moderately soluble in *wood-spirit*, especially when warm. *Ether* dissolves it in somewhat considerable quantity at ordinary temperatures, and still more when heated. Boiling *oil of turpentine* dissolves about $\frac{1}{5}$ of its weight of the acid.

The aqueous solution imparts a deep violet colour to *ferric salts*.

Decompositions.—1. Salicylic acid, when quickly heated, especially if it be impure, gives off phenol (Marchand, Cahours). Heated with pounded glass or quicklime, it is resolved into phenol and carbonic anhydride. (Gerhardt, iv. 389.)

2. Heated with dilute sulphuric acid and *manganic peroxide*, it yields formic acid.

3. *Sulphuric anhydride* converts it into sulphosalicylic acid, $C^7H^6O^3.SO^3$.

4. Fuming *nitric acid* in the cold converts salicylic acid into nitrosalicylic acid; by prolonged action, however, picric acid is produced. The same products are obtained by treating salicylic acid with a mixture of fuming nitric and strong sulphuric acid.

5. With *chlorine* and *bromine*, salicylic acid yields chlorinated or brominated acids, the degree of substitution varying according to the proportions used, and the circumstances of the reaction (p. 156).

6. A mixture of *hydrochloric acid* and *chlorate of potassium* converts it into perchloroquinone (p. 29).

7. Dry salicylic acid (1 at.) distilled with *pentachloride of phosphorus* (2 at. or 3 pts.) yields an oily body, which, after rectifying and collecting the portion which distils between 240° and 270°, consists of salicylic chloride, $(C^7H^4O)''Cl^2$, salicylic chlorohydrate, $C^7H^5O^2.Cl = (C^7H^4O)''\left\{\begin{matrix}Cl\\HO\end{matrix}\right.$ and chlorosalicylic chloride, $C^7H^4Cl^4$, or $(C^7H^4Cl^2)''Cl^2$. The first and third of these bodies are resolved by boiling with water into hydrochloric acid and chlorosalicylic acid, $C^7H^5ClO^2$, isomeric with chlorobenzoic acid; the second yields, in like manner, hydrochloric and salicylic acids.

Such are the results obtained by Kolbe and Lautemann (Jahresb. 1860, p. 288), who however, regard the compound $C^7H^4OCl^2$ as *chloride of chlorosalylic acid*, $C^7H^4ClO.Cl$ (isomeric with chloride of chlorobenzoyl), and the third as *trichloride of chlorosalyl*, $C^7H^4Cl.Cl^3$.

Chiozza (Ann. Ch. Phys. [3] xxxvi. 102; Jahresb. 1852, p. 493), by distilling salicylic acid with pentachloride of phosphorus, had previously obtained an oily distillate, which yielded chlorobenzoic acid (or an isomer) when treated with water. Gerhardt (Ann. Ch. Pharm. lxxxix. 360; Jahresb. 1854, p. 421), by acting in like manner on methylsalicylic acid (oil of wintergreen), obtained salicylic chlorohydrate, $C^7H^5O^2Cl$; and Drion (Jahresb. 1854, p. 423), by the same process, likewise obtained the latter compound, together with salicylic chloride, $C^7H^4OCl^2$. Kekulé (*ibid.* 1860, p. 293), by heating the distillate obtained with wintergreen oil and phosphoric chloride to 180°—200°, to expel oxychloride of phosphorus and the excess of pentachloride (1 at. methylsalicylic acid decomposes only 1 at. PCl^5), obtained a product which, when treated with water, yielded only salicylic acid, no chlorobenzoic or chlorosalylic acid: therefore C^7H^5OCl; but when the chlorinated distillate was further heated to somewhat below 280°, the compound $C^7H^4OCl^2$ was obtained, which yielded with water the chlorinated acid $C^7H^5ClO^2$. Kekulé finds, however, that the composition of the chlorinated distillate is by no means constant, but that the proportion of chlorine increases at each rectification.

Very different results have been obtained by Couper (Ann. Ch. Pharm. cix. 369; Jahresb. 1858, p. 266), who, by gradually dropping 1 at. wintergreen oil into 2 at. pentachloride of phosphorus, and rectifying, obtained a yellowish liquid passing over at about 290°, and a blackish residue which solidified on cooling. This liquid has the composition $C^7H^4Cl^3PO^3$ (*salicyl-trichlorophosphate*), and is resolved by water into hydrochloric, phosphoric, and salicylic acids. Its formation may be represented by the equation:—

$$C^7H^6O^3 \quad + \quad PCl^5 \quad = \quad 2HCl \quad + \quad C^7H^4Cl^3PO^3.$$

8. Dry salicylate of sodium distilled with excess of *phosphoric oxychloride* gives off hydrochloric acid, a viscid liquid which passes over at a high temperature, and on exposure to the air deposits tabular crystals consisting of the phenylic ether of lasylic acid, $C^{13}H^{8}O^2 = \left.\begin{matrix}C^7H^3O\\C^6H^5\end{matrix}\right\}O.$ (Kolbe and Lautemann.)

9. With *chloride of acetyl* salicylic acid forms acetyl-salicylic acid, $C^7H^5(C^2H^3O)O^3$, metameric with terephthalic acid. (H. v. Gilm, Ann. Ch. Pharm. cxii. 180.)

10. Salicylic acid heated with *iodine* yields a mixture of mono-, di-, and tri-iodosalicylic acids (Kolbe and Lautemann), together with tri-iodophenol (Lautemann, Jahresb. 1861, p. 393). The same iodated salicylic acids are produced by dropping tincture of iodine into a cold aqueous solution of salicylate of barium (Kolbe and Lautemann). On adding a solution of iodine in chlorine-water to a warm aqueous solution of salicylic acid, a crystalline precipitate is immediately formed, which after washing with cold water, is found to contain a considerable quantity of an iodine—probably an iodosalicylic acid. (H. Watts.)

SALICYLATES.—Salicylic acid is dibasic, forming acid and neutral salts, represented by the following formulæ:—

$$\text{Acid,} \quad C^7H^5MO^3 = \left.\begin{matrix}(C^7H^4O)''\\HM\end{matrix}\right\}O^2 \text{ and } C^{14}H^{10}M''O^6 = \left.\begin{matrix}(C^7H^4O)^2\\H^2M''\end{matrix}\right\}O^4.$$

$$\text{Neutral,} \quad C^7H^4M^2O^3 = \left.\begin{matrix}(C^7H^4O)''\\M''\end{matrix}\right\}O^2 \text{ and } C^7H^4M''O^3 = \left.\begin{matrix}(C^7H^4O)''\\M''\end{matrix}\right\}O^2.$$

The acid salicylates of diatomic metals may also be regarded as compounds of the neutral salts with the free acid: $C^{14}H^{10}M''O^6 = C^7H^4M''O^3.C^7H^6O^3$. The neutral salicylates of the monatomic metals, potassium, ammonium, and silver, have not been obtained.

Salicylic acid was formerly regarded as monobasic, the salts here considered as acid being then regarded as neutral; indeed, the existence of salicylates containing 2 at. of a monatomic or 1 at. of a diatomic metal was not known till 1855, when several of them were prepared by Piria. The diatomicity of salicylic acid is corroborated by the existence of acid salicylic ethers, oil of wintergreen for example, and by the composition of salicylamic acid and salicylimide (p. 150).

The salicylates of ammonium, potassium, sodium, barium, strontium, magnesium, calcium, and zinc, are soluble and crystallisable. The aqueous solutions of the alkaline salicylates turn brown on exposure to the air. Most salicylates are resolved by dry distillation into phenol and a carbonate.

Salicylate of Ammonium, $C^7H^5(NH^4)O^3$.—Deposited in crystalline scales from a solution of the acid saturated with ammonia, then boiled and evaporated, or in silky needles by spontaneous evaporation of the dilute solution. The crystals are monoclinic (Marignac). It melts at 126° (Procter), and is completely decomposed by distillation into water and salicylamic acid, according to Cahours; according to Limpricht, however, salicylamic acid is not produced in this way.

Salicylates of Barium.—The *acid salt*, $C^{14}H^{10}Ba''O^6.H^2O$, or $C^7H^4Ba''O^3.C^7H^6O^3.H^2O$, is formed by boiling salicylic acid with carbonate of barium, and separates on evaporation in short, concentrically grouped, shining needles, which give off their water at 218° (Cahours). A boiling concentrated solution of this salt mixed with concentrated baryta-water deposits the *neutral salt*, $C^7H^4Ba''O^3.2H^2O$, in small colourless laminæ, which give off their water at 140°. The salt has an alkaline reaction, and is resolved by carbonic acid into the acid salt and carbonate of barium. It dissolves but slightly in water even at the boiling heat. (Piria.)

Salicylates of Calcium.—The *acid salt*, $C^{14}H^{10}Ca''O^6.2H^2O$, prepared like the acid barium-salt, is soluble in cold water, and separates therefrom by spontaneous evaporation in well-developed octahedrons. On mixing a concentrated solution of this salt with a solution of lime in sugar-water containing a large excess of sugar, and warming the liquid in the water-bath, the *neutral calcium-salt*, $C^7H^4Ca''O^3.H^2O$, separates as a sandy insoluble powder, which retains its water at 100°, but gives it off at 180°. It is decomposed by carbonic acid in the same manner as the neutral barium-salt.

Salicylates of Copper.—The *acid salt*, $C^{14}H^{10}Cu''O^6.4H^7O$, remains dissolved when a solution of the acid barium-salt is decomposed by sulphate of copper, and crystallises in long greenish-blue needles, which do not give off their water till heated considerably above 100°. When heated with a quantity of water not sufficient to dissolve it completely, it melts below 100°, and is resolved into salicylic acid and the *neutral copper-salt*, $C^7H^4Cu''O^3.H^2O$, which forms a yellowish-green, light, nearly insoluble powder. The same decomposition of the acid salt is effected by ether. (Piria.)

Potassio-cupric salicylate, $C^{14}H^8Cu''K^2O^6.4H^2O$, is obtained on adding salicylic acid to a solution of cupric tartrate in excess of strong potash-ley, as a light-green crystalline precipitate, which separates from solution in a small quantity of warm water, in emerald-green rhombic plates. It is very soluble in water, insoluble in alcohol and ether, and is resolved by boiling its aqueous solution into cupric oxide and acid salicylate of potassium. It gives off its water below 100°.—*Baryto-cupric salicylate*, $C^{14}H^8Cu''Ba''O^6.4H^2O$, separates on mixing the solution of the preceding salt with chloride of barium, as a siskin-green crystalline precipitate insoluble in water. The water of crystallisation begins to escape at 35°. (Piria.)

Salicylates of Lead.—The *acid salt*, $C^{14}H^{10}Pb''O^6.H^2O$, is obtained by boiling salicylic acid with water and carbonate of lead, in needles having a very brilliant satiny lustre, or by pouring a strong solution of salicylate of ammonium or potassium into a strong solution of acetate of lead, as a white crystalline precipitate, soluble in boiling water (Cahours).—The *neutral salt*, $C^7H^4Pb''O^3$, is obtained as a heavy crystalline powder by adding basic acetate of lead to a boiling saturated solution of the acid salt.—A *basic salt*, $2C^7H^4Pb''O^3.3Pb''O$, separates as a white powder composed of nacreous scales, on boiling the acid salt with a slight excess of ammonia. (Piria.)

Salicylate of Magnesium (acid), obtained by boiling the aqueous acid with magnesia or its carbonate, forms radiating needles often aggregated in a compact mass. It dissolves easily in cold and still more in boiling water. (Cahours.)

Salicylate of Potassium, $2C^7H^5KO^3.H^2O$, is obtained in colourless, shining, silky needles, by saturating the aqueous acid with carbonate of potassium, evaporating to dryness, and treating the residue with strong boiling alcohol. It is converted by chlorine into dichlorosalicylate, and by bromine into **dibromosalicylate of potassium.** Treated with bromine in presence of excess of potash, it yields a red substance resembling sulphide of antimony, insoluble in alcohol, ammonia, and potash, and having the composition of tribromophenol. (Cahours.)

Salicylate of Silver, $C^7H^5AgO^3$, is a white precipitate, which dissolves in a small quantity of boiling water, and separates on cooling in small very brilliant needles. (Cahours.)

Bromosalicylic Acids.

Monobromosalicylic acid, $C^7H^5BrO^3$. (Gerhardt, Ann. Ch. Phys. [3] vii. 217; Cahours, *ibid.* xiii. 99.)—This acid is produced by triturating salicylic acid with a quantity of bromine not sufficient to convert the whole of it. On washing the resulting gummy mass with small quantities of cold alcohol, to extract the unaltered salicylic acid, dissolving the residue in boiling alcohol, and leaving the solution to evaporate, bromosalicylic acid is obtained in colourless prisms having a strong lustre, and somewhat like salicylic acid. It melts when slightly heated; dissolves but sparingly in *water*, even at the boiling heat; pretty readily in *alcohol* and *ether*, especially when warm. It is decomposed by dry distillation. When distilled with fine sand and a small quantity of baryta, it yields thick vapours condensing into a reddish liquid, which by repeated distillation with sand and baryta yields bromophenol: $C^7H^5BrO^3 = C^6H^5BrO + CO^2$.

Bromosalicylic acid forms with ammonia, potash, and soda, crystallisable salts, which are less soluble in water than the salicylates.—It colours ferric salts red, like salicylic acid.

Dibromosalicylic acid, $C^7H^4Br^2O^3$. (Cahours, Ann. Ch. Phys. [3] vii. 102.)—To prepare this acid, pulverised salicylic acid is gradually triturated with excess of bromine as long as any action takes place, and the mixture is left to stand for some hours; the excess of bromine is then washed out with cold water, and the residue dissolved in boiling ammonia. As the solution cools, the ammonium-salt is deposited in slender shining needles. These crystals are dissolved in water; the acid precipitated by hydrochloric acid; the white precipitate washed and dissolved in boiling alcohol, and the solution left to evaporate. Or bromine is dissolved in a concentrated solution of salicylate of potassium, whereupon the liquid becomes heated, and soon deposits crystals of dibromosalicylate of potassium; this salt is decomposed by hydrochloric acid, and the separated acid washed and crystallised from alcohol.

It forms short colourless or slightly reddish needles, which melt at about 150°. It is sparingly soluble in *water*, moderately soluble in *alcohol*, more easily in *ether*. It dissolves in strong *sulphuric acid* at a gentle heat, and is precipitated from the solution by water. Boiling *nitric acid* dissolves it readily, with evolution of bromine and nitrous vapours and formation of picric acid, which crystallises on cooling. When distilled with sand and a small quantity of baryta, it yields dibromophenol.

The dibromosalicylates of ammonium, potassium, and sodium, are even less soluble than the monobromosalicylates. The potassium-salt crystallises from alcohol in shining colourless prisms.

Tribromosalicylic acid, $C^7H^3Br^3O^3$. (Cahours, Ann. Ch. Phys. [3] vii. 104.)—When a mixture of finely pulverised dibromosalicylic acid with excess of bromine is exposed to sunshine for 25 or 30 days, and the resulting crystals are washed with water, and recrystallised from strong alcohol, tribromosalicylic acid is obtained in small yellowish prisms, very hard and friable, insoluble in water, moderately soluble in *alcohol*, very readily in *ether*.

When distilled with sand and a small quantity of baryta, it yields tribromophenol contaminated with a small quantity of oily matter. When boiled with *nitric acid*, it yields bromine-vapours and yellow crystals.

Its compounds with ammonia, potash, and soda are crystallisable, but very sparingly soluble in water. The ammonium-salt forms with silver-salts a precipitate of a deep orange-yellow colour.

Chlorosalicylic Acids.

Only two of these compounds are known, both being produced by the direct action of chlorine on salicylic acid. (Cahours, Ann. Ch. Phys. [3] xiii. 106.)

Monochlorosalicylic acid, $C^7H^5ClO^3$, is produced:—1. By the action of chlorine on excess of salicylic acid, a portion of the acid therefore remaining undecomposed; it is difficult, however, to purify from dichlorosalicylic acid.—2. When chlorine gas is very slowly passed into a concentrated solution of salicylate of potassium, till the liquid, which becomes brown, begins to deposit a dark-green substance; the solution then decomposed by an acid, and the resulting white precipitate washed with water and crystallised from alcohol, slender needles are obtained consisting of chlorosalicylic acid not quite pure.

Dichlorosalicylic acid, $C_7H_4Cl_2O_3$.—This compound is produced by the action of excess of chlorine on salicylic acid. To prepare it, chlorine gas is passed through a concentrated solution of salicylate of potassium as long as the liquid continues to deposit a dark-green body; this substance is washed on a filter with water till the water runs away colourless, then dissolved in boiling water, which is mixed with ⅓ of its volume of alcohol of 36° Bm.; and the needles of the potassium-salt which separate on cooling are repeatedly crystallised from very weak spirit till they become colourless. These crystals are then dissolved in water, the solution mixed with hydrochloric acid, and the resulting white precipitate dissolved in boiling alcohol of 82 per cent.; the solution on cooling yields the acid in needles or in scales, or by spontaneous evaporation in hard, well-formed octahedrons. The acid dissolves sparingly in boiling *water*, and crystallises in slender needles on cooling. It dissolves in gently heated *oil of vitriol*, and separates partially as the liquid cools.

The acid, distilled two or three times with sand and a small quantity of baryta or lime, is completely resolved into carbonic anhydride and dichlorophenol. It dissolves gradually in boiling *nitric acid*, and deposits beautiful yellow laminæ on cooling.

Dichlorosalicylate of ammonium is sparingly soluble in water. The *acid potassium-salt* forms greyish-white needles very much resembling methyl-dichlorosalicylic acid.

Iodosalicylic Acids.

Formation.—1. When tincture of iodine is dropped into a cold aqueous solution of barytic salicylate, $C_7H_4Ba''O_3$, till the yellow colour of the tincture remains permanent, several iodosalicylic acids are formed, which on addition of hydrochloric acid are precipitated together with unaltered salicylic acid. They cannot, however, be separated from one another by water, although their solubility diminishes as the proportion of iodine increases.—2. When 1 at. salicylic acid is fused with 2 at. iodine, and the product is treated with aqueous potash, several iodosalicylic acids are dissolved out, and there remains a red body resembling amorphous phosphorus, which is insoluble in water, alcohol, ether, alkalis, and acids, is not altered by fuming sulphuric acid, but dissolves with red colour in sulphide of carbon; this body appears to be tetriodo-disalicylic acid, $C_{14}H_6I_4O_5$. (Kolbe and Lautemann, Ann. Ch. Pharm. cxv. 157; Jahresb. 1860, p. 291.)

As iodosalicylic acid is reduced by hydriodic acid to salicylic acid even below 100° (p. 152), Kekulé is of opinion that the iodosalicylic acids obtained by fusing salicylic acid with iodine are not directly-formed substitution-products, but are rather formed in the alkaline solution, during the process of separation; perhaps thus:—

$$\underset{\substack{\text{Salicylic}\\\text{acid.}}}{C_7H_6O_3} + I_2 + KHO = \underset{\substack{\text{Mono-iodo-}\\\text{salicylic acid.}}}{C_7H_5IO_3} + KI + H_2O\text{-.}$$

$$\underset{\substack{\text{Salicylic}\\\text{acid.}}}{C_7H_6O_3} + 2I_2 + 2KHO = \underset{\substack{\text{Di-iodosali-}\\\text{cylic acid.}}}{C_7H_4I_2O_3} + 2KI + 2H_2O.$$

$$\underset{\substack{\text{Salicylic}\\\text{acid.}}}{C_7H_6O_3} + 3I_2 + 3KHO = \underset{\substack{\text{Tri-iodo-}\\\text{phenol.}}}{C_6H_3I_3O} + CO_2 + 3KI + 3H_2O.$$

Preparation.—1. Finely pulverised iodine (2 at.) is intimately mixed with salicylic acid (1 at.), and the mixture is heated over a lamp in a wide-bottomed glass vessel, the heat being removed as soon as the fused mass begins to boil. The resulting brown crystalline mass, containing a mixture of mono-, di-, and tri-iodosalicylic acids, with somewhat considerable quantities of tri-iodophenol (iv. 409) and unaltered salicylic acid, is treated with dilute potash, which dissolves everything excepting the red body above mentioned; the filtered alkaline liquid is mixed with hydrochloric acid; and the separated acids are washed with water, which removes nearly all the unaltered salicylic acid. On dissolving the fused residue in excess of sodic carbonate, and neutralising the liquid with hydrochloric acid, the tri-iodophenol, which is soluble only in excess of alkali, separates out; and the filtered liquid yields on evaporation, first, crystals of sodic tri-iodosalicylate, then, on further concentration, satiny needles of sodic di-iodosalicylate, and, lastly, sodic mono-iodosalicylate in small lancet-shaped laminæ. The complete separation and purification of the last two acids is effected by decomposing the sodium-salts with hydrochloric acid, and boiling the separated acids with carbonate of barium, the di-iodosalicylate of barium being very slightly soluble in water, while the mono-iodosalicylate dissolves with moderate facility.—2. A larger product is obtained by dissolving equal weights of salicylic acid and iodine in alcohol of 80 per cent., and boiling the solution for three hours in a flask provided with an upright condensing tube. The brown solution is mixed with water, heated to drive off the alcohol, then supersaturated with carbonate of sodium, and the resulting sodium-salts are further treated as above. (Lautemann, Ann. Ch. Pharm. cxx. 299; Jahresb. 1861, p. 393.)

Mono-iodosalicylic acid, $C^7H^5IO^3$.—This acid, separated from the purified barium-salt by hydrochloric acid, forms a white crystalline mass, slightly soluble in *water*, easily soluble in *alcohol* and *ether*. It crystallises from water acidulated with sulphuric or acetic acid in long silky needles; from alcohol, by slow evaporation, in hard warty groups of needles. It melts at 196°, and, when suddenly heated, is resolved into free iodine, iodophenol, and carbonic anhydride. By boiling with caustic *potash* it is converted into oxysalicylic acid, $C^7H^6O^4$ (iv. 320).

The aqueous and alcoholic solutions of the acid, and likewise the solutions of its salts, colour *ferric chloride* violet.

Iodosalicylate of Ammonium is sparingly soluble in water, and crystallises in needles. —The *barium-salt*, $C^{14}H^8Ba''I^2O^6$, is very soluble in water, and crystallises in rosettes of delicate laminæ, which assume a reddish colour when heated in the moist state.—The *silver-salt* is sparingly soluble, and crystallises in hard grains. (Lautemann.)

Di-iodosalicylic acid, $C^7H^4I^2O^3$, separated from the barium-salt, forms a white amorphous mass, nearly insoluble in *water*, moderately soluble in *alcohol* and *ether*. From water acidulated with sulphuric acid, and from acetic acid, it crystallises like the mono-iodated acid: from alcohol in needle-shaped crystals. It does not melt at 212°, but turns brown from incipient decomposition; when quickly heated, it decomposes with separation of iodine. Boiling *nitric acid* likewise eliminates iodine from it, and probably converts it into dinitrosalicylic acid. By boiling with strong *potash-ley* it is converted into dioxysalicylic or gallic acid, $C^7H^6O^5$, part of which is, however, resolved into carbonic anhydride and dioxyphenic (pyrogallic) acid.—The solutions of di-iodosalicylic acid and its salts colour *ferric chloride* violet.

The di-iodosalicylates are for the most part very sparingly soluble; the most soluble among them is the *sodium-salt*.—The *barium-salt*, $C^{14}H^6I^4Ba''O^6$, crystallises from a moderately concentrated solution, in needles having a satiny lustre. (Lautemann.)

Tri-iodosalicylic acid. $C^7H^3I^3O^3$.—This acid is very difficult to prepare, being very unstable, and apt to split up, during the process of formation by fusing salicylic acid with iodine, into carbonic anhydride and tri-iodophenol. It is insoluble in water, soluble in *alcohol* and *ether*, and crystallises from the former in tufts of needles. It melts at about 157°, with partial decomposition. Alkalis decompose it, abstracting carbonic anhydride and hydriodic acid, and converting it into a red body, $C^6H^2I^2O$.

Tri-iodosalicylate of Sodium is a grey-green mass very slightly soluble in water. (Lautemann.)

Nitrosalicylic Acids.

Two nitro-derivatives of salicylic acid are known,—viz., the mono- and di-nitrated acids.

Mono-nitro-salicylic acid, or simply **Nitrosalicylic acid,** $C^7H^5NO^5 = C^7H^5(NO^2)O^3$. *Indigotic acid. Anilic acid. Nitro-anilic acid. Anilotic acid. Nitrospiroylic acid.* (Chevreul, Ann. Chim. lxxii. 131.—Buff, Ann. Ch. Phys. [2] xxxvii. 160.—Dumas, *ibid.* lxiii. 205; [3] ii. 227. Gerhardt, *ibid.* vii. 325.—Marchand, J. pr. Chem. xxvi. 385.—Piria, Ann. Ch. Pharm. lvi. 35.—Stenhouse, *ibid.* lxx. 253.—H. Major, *Das chem. Laboratorium der Univ. Christiania*, 1854, p. 84.—Gm. xii. 307.—Gerh. iii. 335.)—This acid was first observed by Chevreul among the products of the decomposition of indigo by nitric acid. Gerhardt obtained it by treating salicylic acid with fuming nitric acid. Piria and Major have shown that it is formed, together with helicin, by the action of cold dilute nitric acid upon salicin.

Preparation.—1. From salicylic acid.—Fuming nitric acid acts violently on salicylic acid, converting it into a reddish resinous mass; and on removing the excess of nitric acid by washing with cold water, and dissolving the residue in boiling water, nitrosalicylic acid is deposited in delicate yellowish needles. It may also be prepared by gently heating salicylic acid with very dilute nitric acid. (Gerhardt.)

2. From indigo.—When indigo is gradually added to boiling dilute nitric acid diluted with 10 to 15 times its weight of water, a solution is formed which on cooling deposits nitrosalicylic acid; but the product requires to be purified by several crystallisations, or by transforming it into a lead-salt, and decomposing the latter with sulphydric acid. (Chevreul, Buff, Marchand.)

3. From methyl-nitrosalicylic acid, by boiling with potash, saturating the resulting brown-red liquid with hydrochloric acid, and crystallising the flaky acid which separates. (Cahours.)

Properties.—Nitrosalicylic acid crystallises in colourless needles containing 1 at water, $C^7H^5(NO^2)O^3.H^2O$, which they readily give off on exposure to dry air. It melts at a moderate heat, and solidifies on cooling to a crystalline mass composed of six-sided plates. It reddens litmus, and sublimes at a gentle heat. It is very sparingly soluble in cold *water*, but dissolves easily in boiling water and in *alcohol*. Its solutions are coloured blood-red by ferric salts.

Boiling *nitric acid* converts nitrosalicylic acid into picric acid. A boiling solution of *chloride of lime* converts it into chloropicrin (Stenhouse). By boiling with *hydrochloric acid* and *chlorate of potassium* it is quickly converted into perchloroquinone. The same transformation takes place in a few days when *chlorine gas* is passed into the hot aqueous solution. Nitrosalicylic acid in contact with *nascent hydrogen* dissolves in water, forming a blood-red solution, which gradually deposits purple-red flocks. (Buff.)

Nitrosalicylates, $C^7H^4M(NO^2)O^3$ and $C^{14}H^8M''(NO^2)^2O^6$.—These salts are mostly yellow, take fire when heated, and burn like gunpowder without actual detonation. They redden ferric salts strongly.

The *ammonium-salt*, $C^7H^4(NH^4)(NO^2)O^3$, obtained by saturating the acid with ammonia, crystallises by cooling or spontaneous evaporation in fine needles of a gold or orange-yellow colour.—The *potassium-salt*, $C^7H^4K(NO^2)O^3$, forms yellow silky crystals slightly soluble in cold water, moderately soluble in alcohol.—The *sodium-salt* is yellow, and very soluble in water.

The *barium-salt*, $C^{14}H^8Ba''(NO^2)^2O^6.4H^2O$ (?), obtained by saturating the acid with carbonate of barium, crystallises in shining yellow needles, which are sparingly soluble in cold water, insoluble in alcohol, and give off 12·7 per cent. water of crystallisation at 200°.—A *basic salt*, $C^{14}H^8Ba''(NO^2)^2O^6.Ba''H^2O^2.4H^2O$, is obtained as a yellow powder of the colour of lead-chromate, by precipitating a solution of the preceding salt with ammonia.

The *strontium-*, *calcium-*, and *magnesium-salts* are yellow, and very soluble in water.

The *ferric salt* forms long, dark-red, nearly black needles, which dissolve slowly in water, forming a blood-red solution.

The *neutral lead-salt*, $C^{14}H^8Pb''(NO^2)^2O^6.H^2O$, obtained by saturating the acid with carbonate of lead, or by pouring nitrosalicylate of potassium into a hot solution of a lead-salt, forms a very bulky crystalline precipitate, which increases considerably as the liquid cools.—A *basic lead-salt*, $C^{14}H^8Pb''(NO^2)^2O^6.Pb''O$, is formed when the neutral salt is treated with hot aqueous ammonia; it is a dark-yellow powder, quite insoluble in water, and contains 56 per cent. lead-oxide (Dumas). When a neutral solution of lead-nitrate is poured into a boiling solution of potassic nitrosalicylate, the mixture deposits, after a short time, very slender dark-yellow needles, insoluble in water, and containing 50 per cent. lead-oxide. (Buff.)

The *mercurous salt* is obtained by mixing the solution of potassic nitrosalicylate and barytic nitrate, as a light-yellow precipitate, insoluble in cold, slightly soluble in boiling water.

The *silver-salt*, $C^7H^4Ag(NO^2)O^3$, is obtained by precipitating the ammonium-salt with silver-nitrate, and crystallises easily from boiling water in straw-coloured needles. When heated, it does not detonate, but throws out very bulky vegetations of carbide of silver.

Dinitrosalicylic acid, $C^7H^4N^2O^7 = C^7H^4(NO^2)^2O^3$. *Nitropopulic acid.*—(Cahours, Ann. Ch. Phys. [3] xxv. 11.—Stenhouse, Ann. Ch. Pharm. lxxviii. 1.)—Produced:—1. As an acid methyl-ether, by the action of a mixture of fuming nitric and sulphuric acid on methylsalicylic acid. On boiling the resulting methyl-dinitrosalicylic acid for a few minutes with strong caustic potash, a dipotassic dinitrosalicylate is obtained as a sparingly soluble salt of a splendid red colour; and on treating this salt with strong sulphuric acid, keeping the temperature from rising above 50°, sulphate of potassium is formed, together with dinitrosalicylic acid, which may be dissolved out by cold water. (Cahours.)

2. By digesting the aqueous extract of the branches of certain poplars (*Populus balsamifera, P. nigra*) with dilute nitric acid (Stenhouse). For details of the preparation, see Gmelin's *Handbook*, xii. 314.

Dinitrosalicylic acid crystallises from boiling water in nearly colourless silky needles, or by slow evaporation in small hard prisms. It is very soluble in pure *water*, but only slightly soluble in water containing sulphuric or hydrochloric acid. It dissolves easily in *alcohol* and *ether*. Its taste is very sour at first, then astringent, and finally very bitter. Its solutions impart a persistent yellow colour to the skin. It melts at a moderate temperature, when cautiously heated, and sublimes without alteration.

Dinitrosalicylic acid produces a deep cherry-red colour with *ferric salts*. Strong *nitric acid* at the boiling heat quickly converts it into picric acid (hence, in preparing it from poplar extract, the heat must be kept low). *Oil of vitriol* dissolves it at low temperatures, and water separates it from the solution unaltered; but the mixture carbonises when heated. When heated with *hydrochloric acid* and *chlorate of potassium*, it is converted into perchloroquinone.—*Chloride of lime* does not attack in the cold; but on heating the mixture, a violent action takes place, resulting in the formation of chloropicrin.

Dinitrosalicylates.—Dinitrosalicylic acid forms *neutral salts*, $C^7H^2M^2(NO^2)^2O^3$ and $C^7H^2M''(NO^2)^2O^3$, and *acid salts*, $C^7H^3M(NO^2)^2O^3$ and $C^{14}H^6M''(NO^2)^4O^6$. They are mostly yellow, sparingly soluble, and detonate violently when heated.

The *ammonium-salt*, $C^7H^3(NH^4)(NO^2)^2O^3$, is easily obtained by dissolving the acid in ammonia, and separates on evaporation in small needles of a fine yellow colour.

Potassium-salts.—The *neutral* or *dipotassic salt*, $C^7H^2K^2(NO^2)^2O^3$, is produced when methyl-nitrosalicylic acid is decomposed by boiling with excess of strong potash-ley. It forms beautiful needles having a splendid yellowish-red colour and satiny lustre, and united in stellate groups. It appears to be completely decomposed by continued boiling with potash; detonates violently on glowing coals or on a hot plate (Cahours). The *monopotassic* or *acid salt*, $C^7H^3K(NO^2)^2O^3$, produced by neutralising the aqueous acid with carbonate of potassium (Stenhouse), or by heating the neutral salt with dilute nitric acid (Cahours), crystallises in small lemon-yellow prisms; very sparingly soluble in cold water; insoluble in alcohol or ether. It dissolves very readily in alkaline liquids, and is precipitated therefrom by acids (Stenhouse). It deposits the free acid when boiled with strong hydrochloric acid. It dissolves in slightly heated oil of vitriol, and the solution, on being mixed with water, deposits the acid in crystalline laminæ. It detonates on glowing coals, but not so strongly as the neutral salt.

The *monosodic salt*, $C^7H^3Na(NO^2)^2O^3$, obtained by neutralising the aqueous acid with carbonate of sodium, forms small spicular crystals or yellow shining needles, more soluble in water than the potassium-salt.

Barium-salts. The *neutral salt*, $C^7H^2Ba''(NO^2)^2O^3$, is obtained by adding a boiling solution of caustic baryta to a boiling solution of the acid, as long as the resulting precipitate redissolves on agitation. The filtrate then on cooling deposits small granular crystals.—The *acid-salt*, $C^{14}H^6Ba''(NO^2)^4O^6$, is obtained as a yellow precipitate on adding baryta-water in excess to dinitrosalicylic acid. It is crystalline, and very slightly soluble in boiling water.

The *lead-salt* is very sparingly soluble in water.

The *silver-salt*, $C^7H^3Ag(NO^2)^2O^3$, is obtained, in small granular very slightly soluble crystals, by saturating a hot dilute solution of the acid with carbonate of silver.

Oxysalicylic Acids.

Oxysalicylic acid, $C^7H^6O^4$, and dioxysalicylic acid, $C^7H^6O^5$, are formed by the action of boiling potash-ley on mono- and di-iodosalicylic acid respectively (iv. 320; v. 158).

SALICYLIC ANHYDRIDES. (Gerhardt, Ann. Ch. Phys. [3] xxxvii. 322.)—When dry salicylate of sodium is treated with phosphoric oxychloride, hydrochloric acid is evolved, and two products are formed, both containing the elements of salicylic acid *minus* water, viz.:—

$$\text{Disalicylic acid, } C^{14}H^{10}O^5 = \left.\begin{matrix}(C^7H^4O)'' \\ (C^7H^4O)'' \\ H^2\end{matrix}\right\}O^3 = 2C^7H^6O^3 - H^2O.$$

$$\text{Salicylide} \quad C^7H^4O^2 = (C^7H^4O)''O = C^7H^6O^3 - H^2O.$$

The formation of these compounds may be represented by the equation:—

$$4C^7H^5NaO^3 + PCl^3O = C^{14}H^{10}O^5 + 2C^7H^4O^2 + NaCl + 2HCl + PNa^3O^4.$$

The product of the reaction is a hard mass, which, when heated with water, is converted into a viscous substance soluble in boiling alcohol. The alcoholic solution on cooling deposits disalicylic acid in the form of a thick oil, which very slowly solidifies, and, when treated with boiling water or with alkalis, is converted into salicylic acid. Boiling ether dissolves it, and leaves it on evaporation in the form of a plastic mass.

If salicylic acid be regarded as monobasic, and represented by the formula $C^7H^5O^2.H.O$, disalicylic acid will be its anhydride, $(C^7H^5O^2)^2O$, which is the view of its composition taken by Gerhardt. In like manner, the compounds now denominated salicyl-acetic and salicyl-benzoic acids were formerly regarded as anhydrides (p. 150).

Salicylide, $C^7H^4O^2$, the true anhydride of salicylic acid, is the portion of the above-described product which is insoluble in boiling alcohol. It is white, amorphous, not attacked by boiling water, insoluble in boiling ether. When heated, it melts to a transparent liquid, which solidifies to a translucent mass on cooling. It is not attacked by a boiling solution of sodic carbonate, and but slowly by boiling aqueous ammonia, but potash quickly converts it into salicylate of potassium.

When salicylic anhydride [? disalicylic acid or salicylide] is subjected to dry distillation, the portion which passes over below 300° contains phenol and a body having the composition C^7H^4O [$=$ salicylide, $C^7H^4O^2 - CO$]; and on expelling the phenol by heat, and crystallising the residue from alcohol, with addition of animal charcoal, this body is obtained in silky needles, which melt at 103°, dissolve in 125 pts. alcohol of specific gravity 0·801, and sparingly in water and in ether. The crystals heated with *bromine* to 100° yield a bromine compound, C^6H^3BrO, which melts at 195°, and crystallises from hot alcohol in needles.—A nitro-compound, $C^6H^3(NO^2)O$, crystallising in a similar form, and melting at 150°, is produced by treating the compound C^6H^4O for several days with fuming nitric acid. This nitro-compound is converted by sulphide of ammonium into a base, C^6H^5ON, which crystallises in yellow needles, and forms a crystalline platinum-salt somewhat soluble in water. The compound C^6H^4O yields with strong sulphuric acid a sulpho-acid, which forms a barium-salt crystallising in nodules (H. Marker, Ann. Ch. Pharm. cxxiv. 249). The formation of the compound C^6H^4O was first noticed by Limpricht. (*Lehrb. d. org. Chem.* p. 914.)

SALICYLIC CHLOROHYDRATE. $C^7H^5O^2Cl = (C^7H^4O)''\left\{\begin{matrix}Cl\\HO\end{matrix}\right.$—This body, metameric with chlorosalicylol (p. 171), and commonly called *chloride of salicyl*, is produced, together with chlorobenzoylic chloride, $C^7H^4ClO.Cl$, by the action of pentachloride of phosphorus on methylsalicylic acid (Gerhardt, *Traité*, iii. 343; Drion, Ann. Ch. Pharm. xcii. 423), and on salicylic acid (Kolbe and Lautemann, Jahresb. 1860, p. 288; Kekulé, *ibid.* 293; see also p. 154 of this volume). When separated from phosphoric oxychloride by heating the product to 160°, it forms a slightly-coloured fuming liquid. In contact with water, it becomes heated, and is transformed into hydrochloric and salicylic acids. With methylic and ethylic alcohols, it yields in like manner methyl- and ethyl-salicylic acids. It cannot be distilled without decomposition, hydrochloric acid being then evolved, and a fuming liquid passing over which exhibits all the characters of chlorobenzoylic chloride; a large quantity of carbonaceous matter is also left behind. (Gerhardt.)

SALICYLIC ETHERS. By distilling salicylic acid with an alcohol and strong sulphuric acid, acid ethers are obtained having the composition of salicylic acid in which 1 at. of the typic hydrogen is replaced by an alcohol-radicle, the remaining atom of hydrogen being replaceable by metals, or likewise by alcohol-radicles, yielding neutral salicylic ether.

Methylsalicylic acid, $C^8H^8O^3 = \left.\begin{matrix}(C^7H^4O)''\\CH^3\\H\end{matrix}\right\}O^2$. *Gaultheric acid.* (Cahours, Ann. Ch. Phys. [3] x. 327; xxvii. 5.—Procter, J. Pharm. [3] iii. 27.—Gerhardt, Compt. rend. xxxviii. 32.)—This ether, isomeric with anisic acid, exists ready-formed in the volatile oil of wintergreen (*Gaultheria procumbens*), of which it constitutes about $\frac{9}{10}$, the remainder consisting of a hydrocarbon isomeric with oil of turpentine (ii. 825). On rectifying the commercial oil, the hydrocarbon passes over first at about 200°, and the boiling-point then quickly rises to 222°, at which temperature pure methylsalicylic acid passes over.

Methylsalicylic acid is likewise obtained, unmixed with any hydrocarbon, by distilling with water the bark of the sweet birch (*Betula lenta*); and it may be produced artificially by distilling a mixture of 2 pts. salicylic acid, 2 pts. anhydrous methylic alcohol, and 1 pt. of sulphuric acid specific gravity 1·66; or by treating anhydrous methylic alcohol with salicylic chlorohydrate.

Pure methylsalicylic acid is a colourless oil, having a very penetrating but agreeable odour, and a sweet, cooling, aromatic taste. Specific gravity = 1·18 at 10°. Boiling point 222°. Vapour-density, obs. = 5·42; calc. = 5·719. It is slightly soluble in water, and mixes in all proportions with alcohol and ether. Its aqueous solution is coloured violet by ferric salts. It dissolves *iodine* without decomposing, and forms a brown solution.

Decompositions.—1. When methylsalicylic acid is mixed with strong *nitric acid*, violent spirting takes place, if the mixture is not cooled; but when it is kept cool, methylnitrosalicylic acid is produced (Cahours). By fuming nitric acid, it is converted into methyl-nitrosalicylic acid: by a mixture of fuming nitric acid and oil of vitriol into methyl-dinitrosalicylic acid, or by longer action into methyl-trinitrosalicylic acid (Cahours).—2. *Bromine* added by drops to methylsalicylic acid causes considerable rise of temperature and evolution of hydrobromic acid; the mass, which solidifies on cooling, contains methyl-bromosalicylic and methyl-dibromosalicylic acids, the proportions varying according to the quantity of bromine used. *Chlorine* forms similar products, the quantity of hydrogen replaced never exceeding 2 at., even in sunshine (Procter, Cahours).—3. *Pentachloride of phosphorus* acts violently on the acid, forming salicylic chlorohydrate, methylic chloride, and phosphoric oxychloride:

$$C^7H^5(CH^3)O^3 + PCl^5 = C^7H^5O^2Cl + CH^3Cl + POCl^3.$$

For the results obtained by Couper and by Kekulé, see p. 154.

4. With the *chlorides of benzoyl, cumyl,* and *succinyl,* methylsalicylic acid forms benzoic, cumylic, or succinic methylsalicylate, together with hydrochloric acid, *e.g.*:

$$\underset{\substack{\text{Methylsalicylic}\\ \text{acid.}}}{C^7H^5(CH^3)O^3} + \underset{\substack{\text{Benzoic}\\ \text{chloride.}}}{C^7H^5OCl} = \underset{\substack{\text{Benzoic methyl-}\\ \text{salicylate.}}}{C^7H^4(CH^3)(C^7H^5O)O^3} + HCl.$$

5. By *potash-ley* methylsalicylic acid is resolved, after a few hours at ordinary temperatures, immediately when heated, into salicylic acid and methylic alcohol (Procter, Cahours).—6. Heated with anhydrous *baryta,* it yields carbonate of barium and anisol.—7. With *ammonia,* either gaseous or alcoholic, it forms salicylamic acid and methylic alcohol:

$$\left.\begin{matrix}(C^7H^4O)''\\ CH^3\\ H\end{matrix}\right\}O^2 + NH^3 = \left.\begin{matrix}H^2\\ (C^7H^4O)''\\ H\end{matrix}\right\}\begin{matrix}N\\ O\end{matrix} + \left.\begin{matrix}CH^3\\ H\end{matrix}\right\}O.$$

8. When pieces of *potassium* are dropped into methylsalicylic acid heated to between 30° and 60°, the temperature rises, gas is evolved, and after the addition of a considerable quantity of potassium, the mass solidifies, even if kept at 105°. Soon afterwards it takes fire and leaves a black residue. In one experiment salicylol was produced. (Cahours.)

Methylsalicylates, $C^8H^7MO^3 = \left.\begin{matrix}(C^7H^4O)''\\ CH^3\\ M\end{matrix}\right\}O^2$, the formulæ being doubled for diatomic metals.

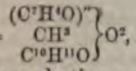
The *potassium-salt*, $C^8H^7KO^3$, is obtained, by agitating strong potash-ley with excess of methylsalicylic acid, in pearly scales, which may be purified by washing with the smallest possible quantity of cold water, pressure between bibulous paper, solution in absolute alcohol, and evaporation *in vacuo*. It then forms extremely delicate white needles, having a strong lustre and resembling asbestos (Cahours): six-sided plates (Procter). It is very soluble in water, alcohol, and ether, colours ferric salts purple, and, when heated in the moist state, gives off methyl-alcohol, and leaves salicylate of potassium. The *sodium-salt* resembles the potassium-salt, but is less soluble in water, alcohol, and ether.—The *barium-salt*, $C^{16}H^{14}Ba''O^6.H^2O$, separates in crystalline scales on gradually adding methylsalicylic acid to hot baryta-water, and leaving the liquid to cool. By dry distillation it is resolved into anisol, carbonate of barium, and carbonic anhydride:

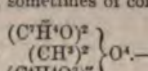
$$C^{16}H^{14}Ba''O^6 + H^2O = 2C^7H^8O + Ba''CO^3 + CO^2.$$

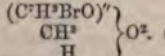
The potassium-salt forms precipitates with the salts of lead, copper, silver, and mercury.

Neutral methylsalicylic ethers,—i.e., compounds in which the basic hydrogen of methylsalicylic acid is replaced by methyl, ethyl, amyl, &c.,—are obtained by heating methylsalicylate of potassium with iodide of methyl, ethyl, or amyl, in sealed tubes. The *methyl-compound*, $C^7H^4(CH^3)^2O^3$, boils at 248°, the *ethyl-compound*, $C^7H^4(CH^3)(C^2H^5)O^3$, at 262°, and the amyl-compound above 300° (Cahours, Compt. rend. xxxix. 256). According to Cahours, these ethers are resolved by boiling with potash into salicylic acid and alcohols; but according to Gräbe (Ann. Ch. Pharm. cxxxvi. 124), the methyl-compound thus treated is converted into methoxysalylic acid, $C^7H^5(CH^3)O^3$, and the ethyl-compound into ethoxysalylic acid. (See SALYLIC ACID.)

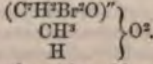
Benzoic methylsalicylate, $C^{15}H^{12}O^4 = \left.\begin{matrix}(C^7H^4O)''\\ CH^3\\ C^7H^5O\end{matrix}\right\}O^2$, is obtained by heating equal parts of methylsalicylic acid and chloride of benzoyl, as long as hydrochloric acid continues to escape, washing the tenacious gradually crystallising product with potash-ley, and crystallising from alcohol or ether.—It crystallises in oblique rhombic prisms having a splendid lustre. They remain unaltered in warm water. When heated with caustic potash, they are strongly attacked, and give off an aromatic odour; and on treating the aqueous solution of the residue with hydrochloric acid, a precipitate of salicylic acid is obtained. The compound is insoluble in water, but dissolves readily in alcohol and ether. (Gerhardt.)

Cumylic methylsalicylate, $C^{18}H^{18}O^4$ =  $\left.\begin{matrix}(C^7H^4O)'' \\ CH^3 \\ C^{10}H^{11}O\end{matrix}\right\}O^2$, is obtained in like manner with chloride of cumyl, but requires for its production a rather higher temperature. The product is a thick oil, which remains liquid for a long time, but, if mixed with a little ether, solidifies on evaporation to a radiated mass. It is insoluble in water, slightly soluble in cold, more soluble in boiling alcohol, whence it crystallises in highly lustrous rhombic scales; very soluble in ether, and separates therefrom by spontaneous evaporation in oblique rhomboidal prisms, sometimes of considerable size.

Succinic methylsalicylate, $C^{20}H^{18}O^8$ =  $\left.\begin{matrix}(C^7\ddot{H}^4O)^2 \\ (CH^3)^2 \\ (C^4H^4O^2)''\end{matrix}\right\}O^4$.—Prepared by gently heating succinic chloride with about 2 pts. of methylsalicylic acid as long as hydrochloric acid continues to escape, digesting the resulting brown mass with potash-ley, and crystallising it from boiling alcohol. The solution on cooling deposits large rectangular laminæ composed of easily separated fibres. The compound is sparingly soluble in ether. (Gerhardt.)

METHYL-BROMOSALICYLIC ACID, $C^8H^7BrO^3$ =  $\left.\begin{matrix}(C^7H^3BrO)'' \\ CH^3 \\ H\end{matrix}\right\}O^2$. (Cahours, Ann. Ch. Phys. [3] x. 339.)—When bromine is slowly dropped into methylsalicylic acid kept as cold as possible, and the mass which solidifies on cooling is freed from hydrobromic acid by washing with weak alcohol and dissolved in boiling alcohol of 36°, the liquid, as it cools, deposits shining crystalline laminæ of methyl-dibromosalicylic acid, an additional quantity of which may be obtained from the mother-liquor on cooling after evaporation to one-half. The remaining mother-liquor, however, yields by further evaporation crystals of methyl-bromosalicylic acid, which may be purified by three crystallisations from alcohol or by sublimation.

Methyl-bromosalicylic acid forms silky needles, having a peculiar odour, melting at 55°, and subliming without decomposition. It is nearly insoluble in *water*, but dissolves readily in *alcohol* and *ether*. It dissolves in cold concentrated *potash-ley*, apparently forming the salt $C^7H^3KBr(CH^3)O^3$; on heating the liquid, methylic alcohol is given off, and bromosalicylate of potassium remains. A strong solution of *ammonia* gradually converts it into bromosalicylamic acid; distilled with *cyanide of mercury* it forms methyl-cyanosalicylic acid.

METHYL-DIBROMOSALICYLIC ACID, $C^7H^6Br^2O^3$ =  $\left.\begin{matrix}(C^7H^2Br^2O)'' \\ CH^3 \\ H\end{matrix}\right\}O^2$. (Cahours, *loc. cit.*)—This acid is prepared, as above described, by the action of bromine on methylsalicylic acid, or by treating the monobrominated acid with excess of bromine. It crystallises from alcohol in rather large prisms, melting at 145°, and volatilising at a higher temperature. It is insoluble in water, but soluble in *alcohol* and *ether*, especially when warm. With *cyanide of mercury* it behaves like the monobrominated compound. It dissolves in *potash* and in *soda*, forming crystallisable salts, from which it is separated by acids in its original state.

Methyl-dibromosalicylic acid is not attacked by excess of bromine, even in direct sunshine.

METHYL-CHLOROSALICYLIC ACID, $C^8H^7ClO^3$, is formed when methylsalicylic acid is exposed to the action of a small quantity of chlorine; but it is difficult to purify. (Cahours.)

METHYL-DICHLOROSALICYLIC ACID, $C^8H^6Cl^2O^3$. (Procter, J. Pharm. [3] iii. 275.—Cahours, Ann. Ch. Phys. [3] x. 343.)—When chlorine gas is passed into methylsalicylic acid till the action ceases, a yellowish crystalline mass is formed, consisting of methyl-dichlorosalicylic acid mixed with a small quantity of liquid methyl-chlorosalicylic acid. By crystallisation from boiling alcohol, the dichlorinated acid is obtained in colourless rhombic tables (Procter); in needles (Cahours). It melts at 104° (Procter), at about 100° (Cahours), and crystallises on cooling; volatilises without decomposition at a stronger heat (Cahours), and sublimes a little above its melting point in rhombic crystals. It is insoluble in water, soluble in *alcohol* and *ether*; dissolves in cold strong caustic *potash*, and is separated therefrom by acids in its original state. It dissolves slowly in *ammonia*, forming a chlorinated amide. When distilled with *cyanide of mercury*, it yields a compound in which the chlorine is replaced by cyanogen. It is not attacked by chlorine in sunshine.

METHYL-NITROSALICYLIC ACID, $C^8H^7NO^5 = \left.\begin{matrix}[C^7H^3(NO^2)O]''\\ CH^3\\ H\end{matrix}\right\}O^2$. *Indigotate of Methylene.* (Cahours, Ann. Ch. Phys. [3] x. 345.)—Produced by adding fuming nitric acid to methylsalicylic acid, cooled so that no spirting may take place. The liquid then quickly solidifies in a crystalline mass, from which the free nitric acid may be extracted by boiling water; and the product, purified by two or three crystallisations from alcohol, forms very delicate yellowish needles, which melt between 88° and 90°, and may for the most part be volatilised without decomposition. It is very slightly soluble in *water*, easily soluble in boiling *alcohol*. *Potash* and *soda* likewise dissolve it easily, forming methyl-nitrosalicylates; *ammonia* ultimately converts it into nitrosalicylamic acid. Boiling potash decomposes it into methylic alcohol and nitrosalicylic acid.

When fuming *nitric acid* in slight excess is gradually added to methyl-nitrosalicylic acid, a brisk action takes place, and a dark-red solution is formed. If the mixture be not cooled, but gently heated at the last, the liquid becomes turbid, and deposits drops of oil, which, if the heat be discontinued as soon as they cease to increase, form a yellow resinous mass; and this substance, when dissolved in hot alcohol, separates almost completely on cooling, in pale-yellow needles, which melt at 95°, and form on cooling a yellow radiated mass, which, if carefully raised to a higher temperature, sublimes in pale-yellow slender needles. It dissolves sparingly and with slight colour in cold water, and more abundantly in hot water, whence it separates in long, slender, nearly colourless crystals; it dissolves also in alcohol and ether, especially when hot. Neither the aqueous solution nor the acid obtained after decomposition with potash reddens ferric salts. The crystals contain 43·40 per cent. C, 9·57 N, and 3·28 H, and are, therefore, a mixture of methyl-nitrosalicylic and methyl-dinitrosalicylic acids (Cahours). Procter obtained a similar substance by boiling wintergreen-oil with nitric acid of specific gravity 1·14.

METHYL-DINITROSALICYLIC ACID, $C^8H^6N^2O^7 = \left.\begin{matrix}[C^7H^2(NO^2)^2O]''\\ CH^3\\ H\end{matrix}\right\}O^2$. *Acide gaulthérique binitrique. Salicylate de methylène binitrique.* (Cahours, Ann. Ch. Phys. [3] xxv. 6.)—When methylsalicylic acid is dropped into a mixture of fuming nitric acid and fuming oil of vitriol kept cool by cold water, a clear dark-orange-coloured liquid is produced. As soon as the drops of methylsalicylic acid cease to dissolve, a small quantity more of nitrosulphuric acid is added, the mixture shaken till the solution is complete, and the liquid, after some minutes, diluted with eight times the quantity of water, whereupon the methyl-dinitrosalicylic acid separates out, and may be crystallised from solution in boiling alcohol. The aqueous mother-liquor contains methyl-trinitrosalicylic acid.

Methyl-dinitrosalicylic acid forms yellowish-white crystalline scales, which become nearly colourless after two crystallisations. It is heavier than water: melts between 124° and 125°, forming a pale-yellowish liquid, which solidifies in a fibrous mass on cooling, volatilises completely when carefully heated in a retort, and sublimes in very delicate shining laminæ. When suddenly heated, it detonates, and decomposes, giving off a thick black smoke, and leaving a carbonaceous residue.

The acid is insoluble in water, even at the boiling heat, nearly insoluble in cold *alcohol*, but easily soluble in boiling alcohol.

It dissolves in gently-heated *oil of vitriol*, and is precipitated therefrom by water in nearly colourless scales, having a strong lustre. The solution in oil of vitriol gives off carbonic anhydride between 75° and 80°: if it be gradually heated, and too great a rise of temperature prevented by frequent immersion in cold water, a colourless liquid is formed, which is rendered turbid by addition of a large quantity of water, and on cooling yields small shining needles, which dissolve readily in boiling water or alcohol, and crystallise on cooling.—If the solution in oil of vitriol be heated somewhat more quickly, or above 100°, the liquid turns red and ultimately black, giving off carbonic and sulphurous anhydrides, and deposits brown flakes when mixed with water.

Methyl-dinitrosalicylic acid dissolves without decomposition in fuming *nitric acid* at temperatures between 30° and 40°, and is reprecipitated by water in its original state. The solution in gently-heated nitromuriatic acid deposits on cooling needles of the unaltered substance.

By continued boiling, either with fuming or with commercial nitric acid, it is completely decomposed, with formation of picric acid. By the continued action of a mixture of nitric and sulphuric acids, it is converted into methyl-trinitrosalicylic acid. By boiling with strong *potash-ley*, it is resolved into methylic alcohol and dinitrosalicylic acid.

Methyl-dinitrosalicylic acid forms salts containing $C^7H^2M(NO^2)^2(CH^3)O^3$. It dissolves in dilute *potash* and *soda*, forming salts which crystallise by evaporation. The *ammonium-salt*, $C^7H^2(NH^4)(CH^3)(NO^2)^2O^3$, obtained by dissolving the acid in a slight excess of warm caustic ammonia, crystallises in yellow transparent needles, sparingly soluble in cold, very soluble in boiling water; the solution, mixed with an acid, deposits methyl-dinitrosalicylic acid. The *silver-salt*, $C^7H^2Ag(CH^3)(NO^2)^2O^3$, obtained by adding nitrate of silver to a dilute solution of the ammonium-salt, is a yellow powder resembling chromate of lead.

METHYL-TRINITROSALICYLIC ACID, $C^8H^5N^3O^9 = \left.\begin{matrix}[C^7H(NO^2)^3O]''\\ CH^3\\ H\end{matrix}\right\}O^2$. (Cahours, Ann. Ch. Phys. [3] xxv. 20.)—When the product of the action of a mixture of strong sulphuric and fuming nitric acid on methylsalicylic acid is treated with boiling alcohol, and the deposit of methyl-dinitrosalicylic acid is separated, the mother-liquor retains methyl-trinitrosalicylic acid, which crystallises in yellowish transparent plates, but always accompanied by picric acid.

Ethylsalicylic acid, $C^9H^{10}O^3 = \left.\begin{matrix}(C^7H^4O)''\\ C^2H^5\\ H\end{matrix}\right\}O^2$. (Cahours, Ann. Ch. Phys. [3] x. 369.—G. Baly, Chem. Soc. Qu. J. ii. 28.—Gerhardt, *Traité*, iii. 326.)—1. When 4 pts. of alcohol are distilled with 3 pts. of crystallised salicylic acid and 2 pts. of oil of vitriol, alcohol alone passes over first, then a mixture of alcohol and ethylsalicylic acid, and lastly a small quantity of alcohol with a large quantity of ethylsalicylic acid. As soon as sulphurous anhydride begins to escape, the distillation is interrupted, the distillate shaken up with water containing a little ammonia, then washed with water, dried over chloride of calcium, and rectified by two distillations. (Cahours, Baly).—2. When absolute alcohol is added by drops to salicylic chlorohydrate, the mixture becomes heated, and gives off large quantities of hydrochloric acid. As soon as the action ceases, the liquid is distilled, and the portion which goes over towards 225° is collected. (Gerhardt.)

Properties.—Ethylsalicylic acid is a colourless oil, heavier than water. Specific gravity 1·097 (Baly); 1·1843 at 10° (Delffs). Boils at 225° (Cahours); at 221° with the barometer at 28″ 1·3‴ (Delffs); at 229·5° (Baly). It has an agreeable odour, resembling that of methylsalicylic acid. It dissolves sparingly in *water*, easily in *alcohol* and *ether*.

Decompositions.—1. *Chlorine* and *bromine* act strongly on ethylsalicylic acid, producing crystallised substitution-products.—2. With *pentachloride of phosphorus* and with *chloride of benzoyl*, it reacts like the corresponding methyl-compound.—3. *Ammonia* dissolves it slowly, converting it into ethylic alcohol and salicylamic acid.—4. *Fuming nitric acid* converts it into ethylic nitrosalicylate; but when boiled with nitric acid, it yields picric acid.—5. When boiled with *potash* or *soda*, it is resolved into alcohol and salicylic acid.—6. Anhydrous *baryta* attacks it strongly, and the product, when distilled, yields ethylic phenate or phenetol:

$$\underset{\text{Ethylsalicylic acid.}}{C^7H^5(C^2H^5)O^3} = CO^2 + \underset{\text{Phenetol.}}{C^6H^5(C^2H^5)O}.$$

Ethylsalicylates.—The acid dissolves in cold potash- or soda-ley, forming crystallised salts soluble in water. Heated in a sealed tube with *methylic*, *ethylic*, or *amylic iodide*, it yields the ethylsalicylate of methyl, ethyl, or amyl.

Benzoic ethylsalicylate, $C^7H^4(C^7H^5O)(C^2H^5)O^3$, is produced by heating the acid with chloride of benzoyl as long as hydrochloric acid continues to escape. It is a crystalline mass, soluble in alcohol and ether, and separates from its ethereal solution by spontaneous evaporation in the form of an oil, which gradually solidifies in nodular groups of small prisms. (Gerhardt.)

ETHYL-BROMOSALICYLIC ACID, $C^7H^4Br(C^2H^5)O^3$, is produced by the action of bromine on salicylic acid in excess. It dissolves very easily in *alcohol*, and crystallises therefrom in slender needles, very much like methyl-bromosalicylic acid. (Cahours, Ann. Ch. Phys. [3] x. 341.)

ETHYL-DIBROMOSALICYLIC ACID, $C^7H^3Br^2(C^2H^5)O^3$, is produced by treating ethylsalicylic acid with excess of bromine. It crystallises in broad nacreous scales, very slightly soluble in cold, moderately soluble in boiling alcohol. It melts at a rather low temperature, and solidifies on cooling in a mass similar to crystallised bismuth; by fusing about 10 or 15 grammes of it, large well-defined cubes may be obtained. When slowly heated, it volatilises almost without residue. It dissolves in strong caustic *potash*, and is precipitated therefrom unaltered by acids. *Ammonia* ultimately dissolves it, forming dibromosalicylamic acid. (Cahours, Ann. Ch. Phys. [3] x. 364.)

ETHYL-DICHLOROSALICYLIC ACID, $C^7H^3Cl^2(C^2H^5)O^3$, **is produced by passing** chlorine into ethylsalicylic acid heated over a water-bath. The solidified mass obtained at the end of the reaction is purified by pressure between bibulous paper, and one or two crystallisations from alcohol, whence it is deposited on cooling in small, colourless, shining plates. (Cahours, Ann. Ch. Phys [3] xxvii. 461.)

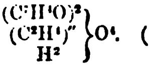
ETHYL-NITROSALICYLIC ACID, $C^9H^9NO^5 = C^7H^4(C^2H^5)(NO^2)O^3$. (Cahours, Ann. Ch. Phys. [3] x. 362.)—When fuming nitric acid is gradually added to ethylsalicylic acid, which is kept cool, a red liquid is formed, from which water throws down a heavy oil, solidifying after a while in a crystalline mass. The oil sometimes remains liquid for several days, but immediately solidifies if a few drops of ammonia are added to saturate the free acid. When the solid mass is repeatedly washed with cold water and dissolved in hot alcohol, the solution yields by evaporation yellow silky crystals, which must be repeatedly recrystallised.

Ethyl-nitrosalicylic acid forms yellowish needles, very much resembling the methyl-compound. It melts in boiling water, and solidifies again on cooling. Heated with *potash* or *soda*, it yields nitrosalicylic acid and alcohol. It is not immediately dissolved by *ammonia*, but when left in contact with it in a closed vessel, it gradually dissolves, forming nitrosalicylamic acid and alcohol.

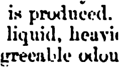
The acid dissolves in cold *potash* or *soda*, forming an ethyl-nitrosalicylate of the alkali-metal.

ETHYL-DINITROSALICYLIC ACID, $C^9H^8N^2O^7 = C^7H^3(C^2H^5)(NO^2)^2O^3$. (Cahours, Ann. Ch. Phys. [3] xxv. 19; xxvii. 462.)—When dinitrosalicylic acid is dissolved in absolute alcohol, and dry hydrochloric acid gas passed into the boiling solution, the liquid evaporated to one-half, and water added, a heavy oil is thrown down which soon solidifies; and if this oil be washed several times with water, and then dissolved in boiling alcohol, the solution on cooling yields crystals of ethyl-dinitrosalicylic acid. The same product is obtained by treating ethylsalicylic acid with nitric and sulphuric acids, in the same manner as methylsalicylic acid is treated for the preparation of methyl-dinitrosalicylic acid (p. 164).

Ethyl-dinitrosalicylic acid forms beautiful yellowish-white scales and plates. It melts at a gentle heat, and solidifies again in the crystalline form on cooling. After being heated for some time, it remains liquid for a considerable time on cooling, and then solidifies in the form of a resin. It forms soluble crystallisable salts with the alkalis. When boiled with *potash*, it is resolved into alcohol and dinitrosalicylic acid.



Ethylene-salicylic acid, $C^{16}H^{14}O^6 = \left.\begin{matrix}(C^7H^4O)^2\\(C^2H^4)''\\H^2\end{matrix}\right\}O^4$. (L. Gilmer, Ann. Ch. Pharm. cxxiii. 277.)—Produced by heating bromide of ethylene with dry salicylate of silver. After purification, it forms white needles, having a fatty lustre, melting at 83°, insoluble in water and in caustic alkalis, soluble in *alcohol*, and precipitated therefrom by ether (Gilmer). According to A. Mayer, on the contrary (Zeitschr. Ch. Pharm. 1864, p. 612), it is more soluble in ether than in alcohol. The laminæ resulting from the first crystallisation are converted by recrystallisation into large colourless or yellowish prisms (Mayer). The compound heated with *pentachloride of phosphorus* gives off hydrochloric acid, phosphoric oxychloride, and chloride of ethylene, and leaves a residue exhibibiting the characters of salicylic anhydride. (Gilmer.)



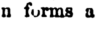
Amylsalicylic acid, $C^{12}H^{16}O^3 = \left.\begin{matrix}(C^7H^4O)''\\C^5H^{11}\\H\end{matrix}\right\}O^2$. (Drion, Ann. Ch. Pharm. xcii. 513.)—Produced by the action of salicylic chlorohydrate on amylic alcohol. It is necessary to operate on small quantities only: otherwise the action becomes too violent, and a large quantity of phenol is produced.

It is a colourless strongly refracting liquid, heavier than water, and insoluble therein, boiling at 270°, and having an agreeable odour. With cold potash-ley, it forms amylsalicylate of potassium. (Drion.)

When boiled with potash, it yields amylic alcohol and salicylate of potassium.

Heated with *chloride of benzoyl*, it gives off hydrochloric acid, and yields a body which crystallises in needles (benzoic amylsalicylate? Gerhardt); according to Drion, it yields a viscid mass, which does not readily solidify.

SALICYLIDE, $C^7H^4O^2$.—The anhydride of salicylic acid (p. 160).



SALICYLIMIDE, $C^7H^5NO = \left.\begin{matrix}(C^7H^4O)''\\H\end{matrix}\right\}N$. (Limpricht, Ann. Ch. Pharm. xcviii. 261.)—Produced by the action of heat on salicylamic acid (p. 150). The residue, obtained by heating the acid to 270°, is washed with cold alcohol, to remove undecomposed salicylamic acid; it then forms a yellow powder, which under the microscope appears to consist of crystalline needles. Does not melt at 200°. It is coloured purple by ferric chloride.

Salicylimide is insoluble in water and in aqueous ammonia, but is dissolved by *alcoholic ammonia*, forming a yellow solution, which, when evaporated, leaves the compound apparently unaltered. Acids decolorise the solution; acetate of lead forms in it a white, nitrate of silver a yellowish, and sulphate of copper a slight greenish precipitate. It is nearly insoluble in boiling *alcohol* and *ether*.

SALICYLOL, $C^7H^6O^2 = (C^7H^4O)''\left\{\begin{matrix}H\\HO\end{matrix}\right.$ *Salicylous Hydride. Hydric Salicylite. Salicylous acid. Hydride of Salicosyl* (incorrectly *Hydride of Salicyl*). *Volatile Oil of Spiræa.* (Pagenstecher, Ann. Ch. Phys. [2] lxix. 331.—Löwig, Pogg. Ann. xxxv. 383.—Piria, Ann. Ch. Pharm. xxix. 300; xxx. 153; lxxxi. 245.—Dumas, *ibid.* xxix. 306.—Löwig and Weidmann, Pogg. Ann. xlvi. 57.—Ettling, Ann. Ch. Pharm. xxix. 309; xxxv. 241; liii. 77.—Wöhler, *ibid.* xxxix. 121.—Marchand, J. pr. Chem. xxvi. 394.—Bertagnini, Ann. Ch. Pharm. lxxxv. 193.)—This compound, intermediate between salicylic acid, $(C^7H^4O)''\left\{\begin{matrix}HO\\HO\end{matrix}\right.$, and the unknown salicylic aldehyde, $(C^7H^4O)''\left\{\begin{matrix}H\\H\end{matrix}\right.$, was formerly regarded as salicylous hydride, or hydride of salicosyl, $C^7H^5O^2.H$. It was discovered in 1835 by Pagenstecher, who obtained it by distilling the flowers of meadow-sweet (*Spiræa Ulmaria*) with water. It appears, however, not to exist ready-formed in these flowers, as it cannot be extracted therefrom by alcohol (Dumas). It is obtained also from the green parts and the rootstock of *Spiræa Ulmaria*; from the green parts of *Sp. digitata*, *Sp. lobata*, and *Sp. filipendula*, but not from the shrubby spiræas (Wicke, Ann. Ch. Pharm. xci. 374); also from the warty secretion of the larvæ of *Chrysomela populi* (Liebig, Schweizer), and, according to Enz (Jahresb. 1859, p. 312), from the beetles themselves by distillation with water.

Artificial formation.—1. By the dry distillation of quinic acid (Wöhler).—2. By the oxidation of saligenin, either in the free state or as contained in salicin or populin; therefore by the action of potassic chromate and sulphuric acid (Piria), or of aqueous osmic acid (Buttlerow, J. pr. Chem. lvi. 278) on saligenin, salicin, or populin, or by the action of bromine or iodine on salicin in water containing potash (Lefort). From saligenin, $C^7H^8O^2$, it is formed by direct oxidation; and as salicin is a glucoside of saligenin (p. 147), and populin has the composition of benzoylsalicin, its formation from these bodies is likewise easily intelligible.—3. By the fermentation of salicin (Ranke, J. pr. Chem. lvi. 1).—4. In the decomposition of helicin (iii. 139), by fermentation, by acids, or by heating with alkalis.

Preparation.—1. From the flowers of *Spiræa Ulmaria*. These flowers distilled with water yield an essential oil, consisting of salicylol mixed with a hydrocarbon having the composition of turpentine-oil, and a camphor-like substance which solidifies at ordinary temperatures. On neutralising this distilled liquid with potash, evaporating nearly to dryness to expel the hydrocarbon (this part of the operation being performed in a retort to keep out the air), then slightly supersaturating the residue with phosphoric acid, and distilling, salicylol passes over, partly as aqueous solution, partly in oil-drops. It may be further purified by repeatedly agitating the last distillate with ether, shaking up the decanted ethereal solution with potash, supersaturating the potash solution with phosphoric acid, and distilling. (Löwig, *Lehrbuch*, ii. 747.)

2. From *salicin*, by oxidation with chromic acid. The best proportions, according to Ettling, are 3 pts. salicin, 3 pts. acid chromate of potassium, 4½ pts. strong sulphuric acid, and 36 pts. water. The potassic chromate is intimately mixed with the salicin; about ⅔ of the water is poured upon the mixture, which is then well agitated in the retort; the whole of the sulphuric acid, diluted with the remainder of the water, is then poured in at once, and the agitation is repeated. A slight evolution of gas then takes place, lasting for half or three-quarters of an hour, the liquid at the same time becoming heated to between 60° and 70°, and assuming an emerald-green colour. As soon as this reaction has ceased, the liquid must be moderately heated. Salicylol then passes over, and condenses in the receiver in the form of a heavy oil, its formation being accompanied by the evolution of carbonic anhydride and formic acid. The distillation is continued till the condensed water is no longer milky. The salicylol dissolved in the water may be extracted by agitating with ether, and evaporating the ethereal solution. The residue in the retort is a solution of chrome-alum, on the surface of which there usually floats a resinous matter, resulting from the decomposition of part of the salicylol. 250 grms. of salicin thus treated yield about 60 grms. of salicylol.

The aqueous extract of willow-bark may also be used instead of pure salicin for the preparation of salicylol. The salicylol thus obtained is purified by combining it with an alkali, concentrating the solution, and distilling it with dilute sulphuric acid.

Properties. Salicylol is a colourless or reddish oil, having a pleasant aromatic odour, like that of bitter-almond oil, and an acrid burning taste. It turns red on exposure to the air, but may be rendered colourless again by a single distillation. Specific gravity = 1·173 at 13·3°. Boiling point, 196·5° (Piria), 182° (Ettling). Vapour-density, obs. = 4·276; calc. = 4·225. It solidifies at − 20°, is inflammable, and burns with a bright but smoky flame.

Salicylol dissolves with moderate facility in *water*; its solution has no action upon litmus; it is coloured deep violet by *ferric salts*. *Alcohol* and *ether* dissolve it in all proportions. The solutions have no action in polarised light.

Salicylol decomposes *alkaline carbonates*, even in the cold. Caustic alkalis dissolve it, with formation of salicylites. When heated with *hydrate of potassium*, it is converted into salicylate of potassium, with evolution of hydrogen:

$$C^7H^6O^2 + KHO = H^2 + C^7H^5KO^3.$$

Ammonia converts it into hydrosalicylamide (iii. 218):

$$3C^7H^6O^2 + 2NH^3 = C^{21}H^{18}N^2O^3 + 3H^2O.$$

By *chlorine* it is converted into chlorosalicylol; by *bromine* into bromosalicylol. *Iodine* dissolves in salicylol without alteration: *nitric acid* converts it into nitrosalicylol; by prolonged boiling with nitric acid, it yields picric acid and carbonic anhydride. Boiled with *hydrochloric acid* and *chlorate of potassium*, it yields perchloroquinone and carbonic anhydride (Hofmann):

$$C^7H^6O^2 + 5Cl^2 + O^2 = C^6Cl^4O^2 + 6HCl + CO^2.$$

By boiling with *acid chromate of potassium* and *dilute sulphuric acid*, it is partly converted into salicylic acid (Ettling). It is likewise oxidised to salicylic acid by boiling with *cupric oxide* in alkaline solution, a precipitate of cupric oxide being formed at the same time. It also reduces *oxide of silver*. When exposed to the vapour of *sulphuric anhydride*, it is converted into a neutral insoluble body, isomeric with salicylol, and related to it in the same manner as benzoin to bitter-almond oil.

COMPOUNDS AND DERIVATIVES OF SALICYLOL.

Salicylol, as already observed, is intermediate in composition between salicylic acid and salicylic aldehyde; and accordingly it forms, on the one hand, salts called salicylites, by exchange of its typic hydrogen for metals, *e.g.* $(C^7H^4O)''\left\{\begin{matrix}K\\HO\end{matrix}\right.$, and, on the other hand, crystalline compounds with acid sulphites of alkali-metals.

These latter compounds are obtained either by direct combination, or by the action of sulphurous anhydride on the salicylites of the alkali-metals:—*Ammonium-salt.*—An aqueous solution of acid sulphite of ammonium easily dissolves salicylol, forming a yellow oily liquid, which after some hours solidifies to a crystalline mass. The product dissolves in hot water, and separates on cooling in shining slightly yellow needles. When exposed to the air for some days, it changes to a brown viscous mass, having a very bitter taste.

Potassium-salt, $C^7H^6O^2.KHSO^3$.—Salicylol shaken up with an aqueous solution of acid potassic sulphite of 28° Bm., dissolves without colour; and the saturated solution solidifies in a few seconds, forming a white inodorous crystalline mass, which may be recrystallised from alcohol. When dry sulphurous anhydride is passed into a cold saturated alcoholic solution of potassic salicylite at a temperature between 40° and 50°, till the yellow colour disappears, and the liquid is then left at rest, it soon becomes filled with slender needles arranged in spherical groups. The compound is white, with a pearly lustre, and a faint odour of salicylol. It dissolves abundantly in cold water, easily in warm alcohol, less easily in cold alcohol. When heated, it gives off sulphurous anhydride and salicylol, leaving a residue of potassic sulphite, which afterwards changes to sulphate. The aqueous solution, when heated, soon becomes turbid, and deposits salicylol; heated with acids, or mixed (even in the cold) with alkalis or alkaline carbonates, it turns yellow, and yields a salicylite. The solution takes up iodine, at first without coloration; when it begins to show colour, the whole of the sulphurous acid is converted into sulphuric acid, and the salicylol is set free. With bromine the solution forms sulphuric acid and bromosalicylol. (Bertagnini.)

Sodium-salt.—A solution of acid sodic sulphite, agitated with a large quantity of salicylol, solidifies to a white crystalline mass, the solution of which in hot water deposits, on cooling, shining crystals, having a sulphurous taste and odour, soluble in pure water; also, with partial decomposition, in boiling alcohol. (Bertagnini.)

Metallicderivatives of Salicylol. Salicylites, $C^7H^5MO^2 = (C^7H^4O)''\left\{\begin{matrix}HO\\M\end{matrix}\right.$ and $C^{14}H^{10}M''O^4 = (C^7H^4O)^2\left\{\begin{matrix}(HO)^2\\M''\end{matrix}\right.$.—These compounds are obtained by the action of salicylol on metallic oxides and hydrates. The salicylites of the alkali-metals are moderately soluble in water; most of the others are insoluble. They are yellow, and contain water of crystallisation. The solutions colour ferric salts violet. In the moist state they quickly decompose, emitting the odour of roses, and turning brown, and ultimately black.

Salicylites of Ammonium.—The *neutral salt*, $C^7H^5(NH^4)O^2$, is obtained by agitating salicylol with strong aqueous ammonia at a gentle heat, and crystallises on cooling in yellow needles. It is slightly soluble in cold water, still less in alcohol; melts at 115°, and volatilises without alteration at a higher temperature. When kept in the moist state in a closed vessel, it gradually decomposes; blackens, becomes semifluid, gives off ammonia, and acquires a very penetrating odour of roses. The alcoholic solution, evaporated with excess of ammonia, yields golden-yellow needles of hydrosalicylamide (Ettling, iii. 219). When macerated with potash or soda, it gives off ammonia only after some time, or when heated. Acids decompose it immediately, separating salicylol. It decomposes the metallic salts of the stronger acids, yielding the ammonium-salt of the acid, and a salicylite of the metal (Löwig and Weidmann). An *acid salicylite of ammonium* is obtained by dissolving the neutral salt in warm water, and adding salicylol; it crystallises, on cooling, in groups of slender, transparent, yellow needles. (Berzelius, *Lehrb.* iv. 350.)

Salicylites of Potassium: α. Neutral, $C^7H^5KO^2$.—1. Potassium dissolves in aqueous salicylol with evolution of hydrogen, forming salicylite of potassium (Löwig).—2. When salicylol is mixed with potash-ley of about 45° Bm., the whole solidifies to a yellow crystalline mass, which separates from the excess of potash-ley; it must be quickly pressed between bibulous paper, and dissolved in a small quantity of hot absolute alcohol, whence the salt crystallises on cooling (Piria).—3. Salicylol is dissolved in three times its bulk of 50 per cent. alcohol, and caustic potash-solution is added till the mass becomes solid; 1 vol. more of the same alcohol is then added, and the whole gently warmed till the solid mass is dissolved. The crystals, which separate on cooling, are washed with a small quantity of cold strong alcohol, whereby they are rendered lighter, then pressed between bibulous paper, and immediately dried *in vacuo* over oil of vitriol (Ettling).—The salt crystallises in small straw-coloured prisms (Löwig); golden-yellow square tables, with a pearly lustre, and unctuous to the touch (Piria, Ettling). It is slightly soluble in water, and has an alkaline reaction. According to Piria, it contains water of crystallisation, which cannot be completely expelled. At 100° it assumes a dark straw-yellow colour, and gives off 10·72 per cent. water (calc. 10·17); and no more at 120°.

It is permanent at ordinary temperatures when dry, but decomposes quickly in the moist state, yielding acetic and melanic acids (iii. 867). When heated, it decomposes with appearance of fire, but without separation of charcoal. (Löwig.)

β. Acid salt, $C^7H^5KO^2.C^7H^6O^2$.—Salicylol is added to the solution of *α* in hot alcohol, till a sample of the liquid on cooling no longer yields tables, but specular crystals; it is then left to cool slowly, and the resulting crystals are washed till the yellow colour disappears. White needles united in tufts, somewhat less alterable than the neutral salt in moist air; decomposes with water into the neutral salt and salicylol. (Ettling.)

Salicylites of Sodium.—The *neutral salt* resembles neutral salicylite of potassium.—The *acid salt*, $2(C^7H^5NaO^2.C^7H^6O^2).H^2O$, prepared like the corresponding potassium-salt, crystallises more readily in slender white needles, which are permanent in the air. At 100° it gives off only 0·007 per cent. water; at 135°, *in vacuo*, 4·036 per cent., and at 140° 4·35 per cent. It bears a temperature of 150° without decomposition, but decomposes at higher temperatures, giving off salicylol. (Ettling.)

Salicylite of Barium, $C^{14}H^{10}Ba''O^4.2H^2O$, separates as a yellow crystalline powder, when chloride of barium is poured into a concentrated solution of potassic salicylite. A hot solution of baryta saturated with salicylol, and left to cool, deposits the same salt in yellow needles. It contains 8·6 per cent. water, which it gives up at 160° in a current of dry air.—The *strontium-* and *calcium-salts* are sparingly soluble.—The *magnesium-salt* is obtained by agitating aqueous salicylol with hydrate of magnesium, as a light-yellow, nearly insoluble powder.

Cupric Salicylite, $C^{14}H^{10}Cu''O^4$, is easily obtained by agitating a cold solution of salicylol in 50 or 60 times its volume of alcohol, with aqueous cupric acetate. The liquid then assumes a fine green colour, and becomes filled, after some time, with iridescent needles of the same colour. These crystals are very slightly soluble in water and in alcohol. An additional quantity of them may be obtained by saturating the acetic acid set free in the reaction with an alkali. An aqueous solution of salicylol shaken up with recently precipitated cupric hydrate, yields a cupric salicylite in the form of a very light powder of a green colour. Cupric salicylite heated to 220° gives off salicylol, benzosalicylol, and carbonic anhydride, leaving a residue of cupric salicylate.

Salicylites of Iron.—The *ferrous salt* is obtained, as a dark-violet precipitate, on adding ammonia to a solution of ferrous chloride mixed with salicylol.—*Ferric salt.* A solution of ferric chloride, mixed with salicylol, immediately assumes a dark-violet colour. The mixture loses its colour on exposure to the air, but recovers it on a fresh addition of salicylol.

Salicylites of Lead.—*a. Neutral.* Recently precipitated hydrate of lead in contact with aqueous salicylol is converted into a light-yellow powder made up of small shining scales.—*β.* A *basic salt*, $C^{14}H^8Pb''O^4.Pb''O$, is precipitated in light-yellow grains, on mixing an alcoholic or aqueous solution of salicylol with basic acetate of lead, or with the neutral acetate and ammonia. With an alcoholic solution of salicylol, the precipitation does not take place immediately. The salt precipitated in the cold is flocculent at first, but gradually becomes crystalline. It is anhydrous.

Mercury-salt.—Mercuric oxide is not attacked by salicylol. A strong solution of mercuric chloride poured upon salicylite of ammonium forms light bulky flocks.

Silver-salt. Obtained by double decomposition, as a yellow precipitate, which soon blackens and decomposes. With very dilute solutions no precipitate is formed; but the sides of the vessel become covered, after about 24 hours, with a pellicle of reduced silver: in a hot solution this reduction takes place immediately. Aqueous salicylol reduces oxide of silver.

Zinc-salt. -Aqueous salicylol shaken up with oxide of zinc, forms a yellow solution, which, when evaporated in a vacuum, leaves a yellow pulverulent residue.

Organic derivatives of Salicylol.—These compounds are formed by the action of salicylol on the chlorides of acid organic radicles.

Acetosalicylol, $C^9H^8O^3 = C^7H^5(C^2H^3O)O^2$. *Acetosalicyl.* (Cahours, Ann. Ch. Pharm. civ. 109; cviii. 312.)—When equal volumes of salicylol and acetic chloride are heated together, the mixture becomes viscous, and evolves large quantities of hydrochloric acid; and if, when this action is over, the liquid be heated for some hours to 100° in a sealed tube, it yields, on slow cooling, brownish prismatic crystals of acetosalicylol, which may be purified by pressure between bibulous paper, and repeated crystallisation from alcohol.

Acetosalicylol is metameric with coumaric acid, $C^9H^7O^2.H.O$, and acetobenzoic anhydride, $C^2H^3O.C^7H^5O.O$. It is insoluble in water, slightly soluble in ether and in cold alcohol, more freely in boiling alcohol, from which it separates almost completely in slender needles.

Anisosalicylol, $C^{15}H^{12}O^4 = C^7H^5.(C^8H^7O^2)O^2$, is produced by treating salicylol with chloride of anisyl. (Cahours.)

Benzosalicylol, $C^{14}H^{10}O^3 = C^7H^5O^2.C^7H^5O$. *Benzosalicyl. Parasalicyl.* (Ettling, Ann. Ch. Pharm. liii. 77.—Cahours, *ibid.* lxxviii. 228; cviii. 312.)—This compound, metameric with benzoic anhydride, $(C^7H^5O)^2O$, and oreoselone, is produced: 1. By the dry distillation of cupric salicylite. On treating the oily distillate, from which crystals have already separated, with potash-ley, the benzosalicylol remains undissolved, and may be crystallised from warm alcohol or ether (Ettling).—2. By the action of benzoic chloride on salicylol. (Cahours.)

Benzosalicylol crystallises in obliquely bevelled triclinic prisms melting at 127°, and forming a pale-yellow liquid, which solidifies to a radiate mass at 98°. At 180° it sublimes in long needles, undecomposed, and without previous ebullition. It is insoluble in water, but dissolves easily in alcohol and ether; also, without decomposition, in gently-warmed sulphuric acid. Hot strong nitric acid dissolves it with evolution of nitrous vapours, and formation of picric acid. With chlorine or bromine in sunshine it forms crystalline products.

Cumosalicylol, $C^{17}H^{16}O^3 = C^7H^5.(C^{10}H^{11}O)O^2$. *Cumosalicyl.*—Produced by treating salicylol with chloride of cumyl. Crystallises in colourless prisms, resembling toluosalicylol. (Cahours.)

Succinosalicylol.—Salicylol treated with chloride of succinyl yields a compound which crystallises in colourless needles.

Toluosalicylol, $C^{15}H^{12}O^3 = C^7H^5(C^8H^7O)O^2$. *Toluosalicyl.*—Prepared by heating together equal volumes of salicylol and toluylic chloride, pressing the resulting brownish mass between bibulous paper, treating it with hot potash-ley and then with water, and crystallising from strong alcohol. It forms shining, colourless, friable, easily fusible prisms, insoluble in cold water, slightly soluble in boiling water and in cold alcohol, more easily in hot alcohol and in ether. It is not decomposed by distillation with hydrate of potassium. Forms crystallisable substitution-products with chlorine, bromine, and fuming nitric acid. (Cahours, Ann. Ch. Pharm. cviii. 312.)

Bromosalicylols. *Monobromosalicylol*, $C^7H^5BrO^2$. *Bromosalicylous Acid.* (Löwig, Pogg. Ann. xxxvi. 383.—Piria, Ann. Ch. Phys. [3] lxix. 281.—Heerlein, J. pr. Chem. xxxii. 65.)—Produced by adding bromine-water, not in excess, to an alcoholic solution of salicylol, and separates, on addition of water to the liquid, in small colourless needles. It is less fusible than the corresponding chlorine-compound, sublimable, and distils over with vapour of water. It dissolves in *alkalis*, yielding metallic bromosalicylites.

Bromosalicylol forms, with the *acid sulphites of the alkali-metals*, crystalline compounds, which are decomposed by prolonged boiling, or by heating with acids. The *potassium-salt* crystallises in small, colourless, shining needles; the *sodium-salt* in interlaced needles.

Dibromosalicylol, $C^7H^4Br^2O^2$.—Obtained by treating salicylol with excess of bromine-water. It forms long yellowish needles, insoluble in water, soluble in alcohol and in ether. With potash it yields potassic dibromosalicylite; sulphydric acid converts it into the sulphydrate of sulphodibromosalicylol. (Heerlein.)

Chlorosalicylols. *Monochlorosalicylol*, $C^7H^5ClO^2$. *Chlorosalicylous Acid.* (Löwig, Piria, *loc. cit.*)—Salicylol is strongly attacked by chlorine; and if, after the evolution of hydrochloric acid has ceased, a current of dry air be passed through the liquid, chlorosalicylol remains as a yellow crystalline body, which dissolves in boiling alcohol, and crystallises on cooling in colourless, nacreous, rectangular plates. It has an unpleasant odour and burning peppery taste; melts when heated, and sublimes in long snow-white needles; it is inflammable, and burns with a green flame. It is insoluble in *water*, but soluble in *alcohol* and *ether*. It dissolves in strong *sulphuric acid* with yellow colour, and is precipitated from the solution by water. With *ammonia* it forms hydrochlorosalicylamide, $C^{21}H^{15}Cl^3N^2O^3 = 3C^7H^5ClO^2 + 2NH^3 - 3H^2O$ (iii. 219).

Chlorosalicylol dissolves easily in *alkalis*, forming metallic chlorosalicylites. The *potassium-salt* crystallises in radiate groups of red scales. Its solution treated with chloride of barium, yields *barytic chlorosalicylite*, $C^{14}H^8Ba''Cl^2O^4.H^2O$, in the form of a yellow crystalline powder.

Chlorosalicylol dissolves easily also in the *acid sulphites of the alkali-metals*, forming crystalline compounds.

Dichlorosalicylol, $C^7H^4Cl^2O^2$? is produced, according to Löwig, by the prolonged action of chlorine on salicylol. On removing the excess of chlorine by exact saturation with ammonia, agitating the liquid with ether, and evaporating the ethereal solution, a soft red body remains, having a pungent odour, melting at 25°, and forming red salts with the alkalis and alkaline earths. It gave by analysis 39·8 per cent. carbon, 2·4 hydrogen, and 37·1 chlorine, whence Löwig supposes it to be dichlorosalicylol, the formula of which requires 44·0 per cent. carbon, 2·1 hydrogen, 37·1 chlorine, and 20·7 oxygen; but it evidently requires further examination.

Cyanosalicylol, $C^8H^5NO^2 = C^7H^5(CN)O^2$.—This compound, metameric with isatin, is produced by the action of bromide of cyanogen, dissolved in absolute alcohol, on salicylite of potassium. Bromide of potassium then separates, and the alcoholic solution yields by evaporation yellowish crystalline scales of cyanosalicylol, which is a weak base capable of uniting with acids. (Cahours, Ann. Ch. Pharm. cviii. 322.)

Iodosalicylol, $C^7H^5IO^2$?—Iodine dissolves in salicylol without alteration; but by distilling a mixture of potassic iodide and chlorosalicylol, chloride of potassium is obtained, together with a brown sublimate analogous in properties to chlorosalicylol. (Löwig.)

Nitrosalicylol, $C^7H^5NO^4 = C^7H^4(NO^2)O^2$. *Nitrosalicylous Acid. Spiroylic Acid.* (Löwig, *loc. cit.*)—Prepared by treating salicylol, at a gentle heat, with moderately strong nitric acid. It crystallises in transparent yellow prisms, slightly soluble in water, very soluble in alcohol and in ether; its solution imparts a persistent yellow stain to the skin. It melts when heated, and solidifies to a crystalline mass on cooling; sublimes partially at a higher temperature.

Nitrosalicylol dissolves easily in alkalis, forming crystallisable salts. When saturated with *ammonia*, it forms a blood-red liquid, leaving, on evaporation, a yellow residue, from which potash eliminates ammonia, even in the cold. The solution of the sodium-salt forms a yellow precipitate with *lead-salts*, a green precipitate with *cupric salts*, and imparts to *ferric chloride* a deep cherry colour. These salts explode when heated.

Nitrosalicylol unites with acid sulphites of alkali-metals. The *ammonium-salt* does not appear to crystallise. The *potassium-salt* is more soluble than the sodium-salt.—The *sodium-salt*, obtained by dissolving nitrosalicylol in a warm solution of acid sulphite of sodium, crystallises on cooling in golden-yellow interlaced needles, soluble in water, insoluble in alcohol.

Sulphosalicylol, C^7H^6OS. *Thiosalicol.* (Cahours, Compt. rend. xxv. 458.)—This body, which has the composition of salicylol in which half the oxygen is replaced by sulphur, is produced by the action of sulphydric acid on hydrosalicylamide in alcoholic solution. It is a pulverulent substance, which forms salts with the alkalis, and colours ferric salts violet-red.

Bromosulphosalicylol, C^7H^5BrOS, is obtained by the action of sulphydrate of ammonium on bromosalicylol, as a brown resinous substance, soluble in potash.—When sulphydric acid gas is passed into an alcoholic solution of dibromosalicylol and water is thus added, a resinous body is precipitated, consisting of sulphydrate of dibromosulphosalicylol, $C^7H^4Br^2SO.H^2S$.

SALICYL-SULPHURIC ACID. $C^7H^6SO^6$. Syn. with SULPHOSALICYLIC ACID.

SALICYLURIC ACID. $C^9H^9NO^4 = \left.\begin{matrix}H^2\\(C^7H^4O)''\\(C^2H^2O)''\\H\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$. (Bertagnini, *Il Nuovo Cimento*, i. 363.)—This acid, related to salicylic acid in the same manner as hippuric to benzoic acid (iii. 156), is found in the urine after salicylic acid has been swallowed. To prepare it, the acid urine voided after taking salicylic acid is evaporated down to 12° Bm., acidulated with hydrochloric acid, shaken up with ether, and the ether is distilled from the ethereal solution. The residue yields, by spontaneous evaporation, large crystalline nodules, which, when freed from the mother-liquor by pressure, dissolved in boiling water, and treated with animal charcoal, yield a crystalline mass, consisting for the most part of slender needles, mixed with larger needles of salicylic acid. On heating this mixture in a current of air to between 140° and 150°, the salicylic acid volatilises; and the residue, crystallised from hot water containing animal charcoal, yields pure salicyluric acid.

This body crystallises in slender, shining, crystalline needles, which when obtained from the aqueous solution are grouped concentrically. It has a somewhat bitter taste, and a strong acid reaction: melts at about 160°, and solidifies in the crystalline form. It dissolves easily in boiling water and in alcohol, less easily in cold water and in ether. The solutions colour ferric salts violet, like salicylic acid.

Decompositions.—1. Between 160° and 170°, the acid turns brown, and begins to decompose, yielding a sublimate of salicylic acid. At a stronger heat, it swells up and gives off ammonia, leaving a residue of charcoal.—2. When boiled with excess of baryta-water, it does not form any salicylate of barium; a small quantity of ammonia is, however, given off.—3. Heated for a short time with fuming hydrochloric acid, it dissolves, and crystallises out again unaltered; but if the boiling be continued for two or three hours, the acid is resolved into salicylic acid and glycocine:

$$\left.\begin{matrix}H^2\\(C^7H^4O)''\\(C^2H^2O)''\\H\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix} + H^2O = \left.\begin{matrix}(C^7H^4O)''\\H^2\end{matrix}\right\}O^2 + \left.\begin{matrix}H^2\\(C^2H^2O)''\\H\end{matrix}\right\}\begin{matrix}N\\O.\end{matrix}$$

4. When it is boiled with water and peroxide of lead, the latter is decolorised; and on boiling the solution, small shining needles separate out.

Salicylurates.—The acid decomposes carbonates. Its salts crystallise easily.

The *barium-salt* is obtained by dissolving carbonate of barium in the warm acid. As the solution cools, the salt crystallises in large hard prisms, which become opaque and give off water when heated, then melt and decompose, giving off ammonia and an oil which smells like phenol, and leaving a residue of barytic carbonate. The salt is sparingly soluble in cold water.

Calcium-salt.—*a.* When carbonate of calcium is dissolved in the aqueous acid, the solution on cooling yields aggregated needles, which are sparingly soluble in cold water, and insoluble in alcohol.—*b.* When milk of lime is added by successive small portions to the warm aqueous acid, a solution is at first obtained, which suddenly solidifies to a crystalline mass, insoluble in boiling water.

SALIGENIN, $C^7H^8O^2$, probably $= \left.\begin{matrix}(C^7H^6)''\\H^2\end{matrix}\right\}O^2$.—(Piria, Ann. Ch. Pharm. lvi. 53; lxxxi. 245.—Beilstein and Seelheim, *ibid.* cxvii. 83.—Gm. xii. 233.)—A compound produced from salicin by the action of acids and of emulsin (Piria):

$$\underset{\text{Salicin.}}{C^{13}H^{18}O^{7}} + H^{2}O = \underset{\text{Saligenin.}}{C^{7}H^{8}O^{2}} + \underset{\text{Glucose.}}{C^{6}H^{12}O^{6}}.$$

Also from salicylol, $C^{7}H^{6}O^{2}$, by the action of sodium-amalgam in presence of water. (Reinecke and Beilstein, Ann. Ch. Pharm. cxxviii. 179.)

Preparation.—1. An aqueous solution of salicin, acidulated with sulphuric or hydrochloric acid, is heated till it just boils up; the liquid is then saturated with chalk, and the filtrate shaken with ether, which takes up the saligenin. A considerable quantity of saliretin is always formed at the same time.—2. When 50 pts. of finely pulverised salicin suspended in 500 pts. of water are shaken up with 3 pts. of emulsin (ii. 486), and heated in lukewarm water to a temperature not exceeding 40°, the salicin dissolves, being decomposed in the course of 24 hours into glucose and saligenin. When no more than the prescribed quantity of water is employed, part of the saligenin crystallises out; and if the liquid be then twice shaken up with an equal bulk of ether, and the ethereal liquid evaporated over the water-bath, the residue solidifies in a white mass composed of pearly laminæ, which may be pressed between paper, and repeatedly crystallised from boiling water (Piria). Beilstein and Seelheim purify it by recrystallisation from benzene.

Properties.—Saligenin crystallises in white rhombic tables having a pearly lustre, or in small colourless rhombohedrons. By spontaneous evaporation of the aqueous solution, there is formed a white opaque mass, composed of microscopic, shining, iridescent laminæ (Piria). Specific gravity = 1·1613 at 25° (Beilstein and Seelheim). Saligenin is unctuous to the touch. In vacuo over oil of vitriol, it does not give off water, but partly volatilises, in consequence of which the oil of vitriol becomes covered with a crimson crust.—It melts when heated, forming a colourless transparent liquid, which solidifies to a crystalline crust at 82°. When heated for some time to 100°, it yields a sublimate of delicate, white, shining, iridescent luminæ.—The aqueous solution imparts a bright indigo colour to ferric salts. (Piria.)

Saligenin dissolves in 15 pts. of *water* at 22°, and in all proportions of boiling water; easily also in *alcohol* and *ether* (Piria). One part of saligenin dissolves in 52·5 pts. of *benzene* at 18°, and in a much smaller quantity at the boiling heat (Beilstein and Seelheim). The solutions do not act on polarised light. It dissolves in *ammonia*, and appears to combine with potash. The aqueous solution does not precipitate the salts of barium, calcium, copper, neutral lead-acetate, mercuric chloride, nitrate of silver, or tartar-emetic. With basic acetate of lead, it forms a scanty precipitate, of variable composition. It imparts to ferric salts a bright indigo colour, which is quickly destroyed by heat, or by the action of chlorine or acids. The alcoholic and ethereal solutions do not exhibit this colouring.

Decompositions.—1. Saligenin heated above 100° gives off aqueous vapour and salicylol. Between 140° and 150°, it becomes very viscid, and solidifies on cooling to a mass, which is less crystalline the more strongly it has been heated; and at length there is formed an amber-coloured translucent resin having the properties of saliretin.—2. Exposed to the air in contact with *platinum-black*, it is quickly converted into salicylol; at higher temperatures the same conversion is produced by mere contact with the air, or by *chromic acid*, *oxide of silver*, &c., without the formation of any other organic substance or of carbonic anhydride:

$$C^{7}H^{8}O^{2} + O = C^{7}H^{6}O^{2} + H^{2}O.$$

Mercuric oxide does not act upon saligenin.—When saligenin is heated with *sulphuric acid* and *peroxide of manganese*, carbonic anhydride and formic acid are produced, without a trace of salicylol.—3. *Chlorine gas* acts violently on dry saligenin, giving off hydrochloric acid and forming a yellow resin, which gradually turns red, and ultimately solidifies to a mass composed of small crystals, which melt and turn red when exposed to the further action of chlorine. *Bromine* acts in a similar manner.—The chief product formed by the action of chlorine gas on a concentrated aqueous solution of saligenin, is trichlorophenic acid (iv. 392).—4. With *iodine* and *phosphorus* saligenin forms a brown liquid, which appears to contain $C^{7}H^{6}O.IH$, but is very unstable (Limpricht).—5. Saligenin heated with *dilute acids*, is resolved into saliretin and water: $C^{7}H^{8}O^{2} = C^{7}H^{6}O + H^{2}O$.—6. Strong *sulphuric acid* colours saligenin deep red, like salicin.—7. Strong *nitric acid* dissolves it, with evolution of nitrous vapours and carbonic anhydride, and formation of picric acid. Dilute nitric acid converts it into salicylol, partly also into yellow crystals of nitrosalicylol (p. 172).—8. Saligenin is not perceptibly altered by *potash-ley* at ordinary temperatures, but appears to unite with it. When heated with solid *potassic hydrate*, it gives off hydrogen, and forms salicylate of potassium:

$$C^{7}H^{8}O^{2} + KHO = C^{7}H^{5}KO^{3} + 2H^{2}.$$

9. *Sodium* acts upon saligenin dissolved in pure ether, with evolution of hydrogen, and

formation of a precipitate, consisting of the sodium-compound $C^{14}H^{15}NaO^4$. A solution of saligenin in benzene reacts with sodium in a similar manner, excepting that the precipitate formed is not of constant composition (**Beilstein and Seelheim**).—10. *Pentachloride of phosphorus* converts saligenin into saliretin, with evolution of hydrochloric acid and phosphoric oxychloride (**Beilstein and Seelheim**):

$$C^7H^8O^2 + PCl^5 = 2HCl + POCl^3 + C^7H^6O.$$

—11. Saligenin is also converted into saliretin by heating to 100° with acetic anhydride and ether; also when hydrochloric acid gas is passed into a solution of saligenin in glacial acetic acid (**Beilstein and Seelheim**).—12. Saligenin is attacked by *chloride of benzoyl*, with evolution of hydrochloric acid, and formation of a compound containing $C^7H^7(C^7H^5O)O^2$, apparently analogous to the compound ethers. (**Limpricht.**)

Chlorosaligenins. These compounds are produced by the action of emulsin on the corresponding chlorosalicins (p. 149). They are all, like saligenin itself, converted into resinous matters by contact with acids.

Monochlorosaligenin, $C^7H^7ClO^2$, crystallises from hot water in pure colourless rhomboidal plates, exactly like saligenin. It dissolves in water, alcohol, and ether, turns ferric salts blue, and is changed into a resin (? *chlorosaliretin*), under the influence of acids. (**Piria.**)

Dichlorosaligenin, $C^7H^6Cl^2O^2$, and *Perchlorosaligenin*, $C^7H^5Cl^3O^2$, are produced in like manner from di- and per-chlorosalicin, but only in very small quantities. (**Piria.**)

SALIGLYCIC ACID. Syn. with SALICYLURIC ACID.

SALIRETIN. C^7H^6O. (**Piria**, Ann. Ch. Pharm. xxx. 178, 189; lvi. 45.—**Gerhardt**, Ann. Ch. Phys. [3] vii. 215.)—This body, which differs from saligenin by the elements of 1 at. water, is produced by the action of dilute acids on saligenin, or on salicin, glucose being also formed in the latter case. The transformation is effected by the greater number of acids, even in very dilute solution, provided the liquid be heated to the boiling-point. The saliretin then rises to the surface in the form of a resinous body, generally yellowish, sometimes quite white. In general, the more dilute the acid (sulphuric or hydrochloric) employed, the purer is the product obtained. It may be further purified by solution in alcohol and precipitation with water. According to Piria, 100 pts. saligenin treated with dilute hydrochloric acid, and heated to between 120° and 130°, lose 15·39 per cent. water (calc. 14·52 per cent.).

Saliretin is insoluble in water and ammonia, but soluble in alcohol, ether, and strong acetic acid, and is precipitated from these solutions by water. Potash and soda likewise dissolve it, and the solutions are not precipitated by water; but acids (even carbonic acid) separate the saliretin in the form of a white gelatinous pulp. Sulphuric acid colours saliretin blood-red. Strong nitric acid converts it at the boiling heat into picric acid, without formation of oxalic acid. By dry distillation it yields phenol, water, and a copious residue of charcoal.

SALISBURIA. The fruit of *Salisburia adiantifolia* (or *Gingko biloba*) contains, besides gum, sugar, pectin, citric acid, butyric acid, &c., 9 per cent. of a fatty oil which is extracted from it by ether. This oil is yellow, has an acid reaction, solidifies in the crystalline state at 0°, contains a fatty acid, $C^{24}H^{48}O^2$, melting at 35°, and called by **Schwarzenbach** (Jahresb. 1857, p. 529), **gingkoic acid**.—The fleshy part of the fruit contains 74·6 per cent. water, 24·3 dry organic matter, and 1·1 ash.

SALITE. Syn. with SAHLITE.

SALITHOL. Syn. with ETHYLIC PHENATE or PHENETOL (iv. 391).

SALIVA. (**Lehmann**, Lehrb. ii. 9.—**Gorup-Besanez**, *Lehrb.* 433.—**Bidder u. Schmidt**, *Verdauungssäfte*, p. 1.—**Bernard**, *Leçons Phys. Exp.* 1856, vol. ii.—**B. Eckhard**, *Beiträge*, ii. 205.—**Ordenstein**, *ibid.* p. 101.—**Oehl**, *Saliva umana*, 1864.—**Kühne**, *Lehrb. Phys. Chem.* p. 1.)

Several organs—viz., the parotid, submaxillary, sublingual, and buccal glands—pour into the mouth their respective secretions, which, mixed together, form what is called mixed saliva, or briefly saliva.

Parotid Saliva, or the secretion of the parotid gland, may readily be obtained by canalization of the Stensonian duct. The quantity secreted by one gland, in man, has been estimated, for the 24 hours, at 1·4 grm. per kilo of body-weight (**Oehl**). The first drops, obtained after introducing the tube, are turbid and acid, probably from decomposing epithelium; the secretion afterwards flows clear and alkaline. On standing, it becomes turbid, with deposition of carbonate of calcium, probably owing to escape of carbonic acid. **Oehl** states that the fluid, as it escapes from the tube, is often acid, especially when the subject is fasting; he also maintains, that transparency belongs to the acid secretion only, an alkaline or a neutral saliva being always turbid, even as it flows from the tube. There are no special morphotic constituents. Specific gravity (man) 1·0031—1·0043; solid residue, ·571—·616 per cent. Bidder and Schmidt found, in the dog, in 1000 pts. water, 995·3, solids 4·7, of which organic matters 1·4, salts 3·3 (potassic and sodic chlorides 2·1, calcic carbonate 1·2). Parotid saliva is free from mucin, contains a very small quantity of globulin, and a larger but still small amount of albumin. In the horse, Bernard found a material separable by saturation with magnesian sulphate (? globulin). In man, sulphocyanate of potassium is invariably (?) found (to the extent of ·03 per cent.) (Oehl). Bromides and iodides pass readily from the blood into saliva, apparently being substituted for the chlorides, which are proportionately lessened.

Submaxillary Saliva, which flows into the mouth through the Whartonian duct, is a generally transparent, but sometimes turbid, and always more or less viscid fluid, of distinct alkaline reaction, and of very variable specific gravity. Bidder and Schmidt found in the dog, in 1000 pts.—water, 991·45; solids, 8·55: of which organic matters 2·89, salts 5·66 (potassic and sodic chlorides 4·50, calcic and magnesian carbonates and phosphates 1·16). When obtained by canalization, it is limpid as it flows from the tube, but almost immediately becomes viscid. Besides mucin, to which constituent the viscidity is due, it contains a small quantity of globulin and of albumin. In man, according to Oehl, it gives faintly the reactions of sulphocyanate of potassium.

The submaxillary gland is subject to the influence of different systems of nerves, and the quality of the secretion depends on the kind and degree of nervous action set going. Excitation of the *chorda tympani*, and excitation of the *sympathetic* nerve belonging to the gland, produce two distinct kinds of saliva. The chorda-saliva is transparent, distinctly alkaline, free from morphotic constituents, moderately viscid, of specific gravity 1·0039—1·0056, and yields 1·2—1·4 per cent. solid residue. The sympathetic saliva is always turbid or opaque, extremely viscid, and contains peculiar gelatinous microscopical masses, of variable size. There are also other varieties of submaxillary saliva, which have not as yet been closely studied.

Sublingual Saliva is alkaline, exceedingly viscid, with a solid residue of 9·98 per cent., and contains sulphocyanate of potassium.

Buccal Saliva, or *Oral Mucus*, obtained by ligaturing the ducts of all the other salivary glands, is very viscid, and abounds in morphotic constituents—viz. epithelium, with mucus, and the so-called salivary corpuscles. In 1000 pts. Bidder and Schmidt found 9·98 solid residue, of which organic matters 3·84, inorganic matters 6·13.

Mixed Saliva varies in its qualities, according as one or other of its component secretions preponderates. It is generally alkaline, but sometimes acid, probably from acid fermentation of saccharine aliment retained in the cavities and folds of the mouth. The total quantity secreted in the 24 hours varies exceedingly; Bidder and Schmidt calculate it, for man, at 1400 grms.; Lehmann at 473 grms.

Uses of Saliva.—By virtue of its fluidity and viscidity, saliva is of great assistance in mastication and deglutition. Animals, when the ducts of the salivary glands are ligatured, chew and swallow with great difficulty.

When raw starch is exposed at 35° to human saliva, frequently renewed, the starch-granulose is after a while dissolved, and finally converted into dextrin and sugar. Boiled starch treated in the same way is almost instantaneously converted into dextrin and sugar.

In man, parotid and submaxillary saliva, or infusions of the respective glands, possess equally with mixed saliva this power over starch. In the dog, the sympathetic submaxillary saliva alone acts on starch, and that very feebly (Kühne). In the pig, rabbit, and guinea-pig, infusions of the salivary glands, and probably also their secretions, are as energetic as in man. In the horse, the ox, the sheep, and the cat, the secretions and glandular infusions are entirely or almost entirely inactive. In man the change effected by saliva on boiled starch is sufficiently rapid to allow of a considerable production of sugar during the act of mastication. But it is evident that in many animals the saliva can have no such function.

Ptyalin.—This action of saliva on starch is not due to the morphotic elements, to mucus, to the globulin, or to the other albuminoid constituents, but seems to belong to a special "active principle" or "ferment," for which the name ptyalin may be profitably reserved. If saliva be treated, first with dilute phosphoric acid, and then with lime-water, the bulky precipitate of phosphate of calcium carries down with it the greater part of the ferment, together with albumin. If the separated deposit be agitated with distilled water, it gives up the ferment but not the albumin: hence by filtration a clear liquid is obtained, acting powerfully on starch, but free from albumin. From this the ferment may be precipitated by alcohol, forming, when carefully dried, an amorphous powder (mixed with phosphates), containing nitrogen, but not exhibiting the xanthoproteic reaction. (Cohnheim.)

Ptyalin is most active in a neutral or faintly alkaline solution; the addition of an acid, or an alkali, first delays, then arrests, and finally destroys its action. It is most active at a temperature of about 35°; its properties are wholly destroyed when its solution is boiled. The presence of an excess of glucose hinders its action.

M.F.

SALLOW-THORN, or **SEA-BUCKTHORN.** *Hippophaë rhamnoides* (ii. 155).

SALMIAC. Syn. with SAL-AMMONIAC, or CHLORIDE OF AMMONIUM.

SALMONIC ACID. *Salmsäure. Lachssäure.*—A reddish fatty acid, existing, according to Frémy and Valenciennes (J. Pharm. [3] xxviii. 401), in the reddish muscles of various species of salmon, most abundantly in *Salmo salmo* and *S. hamatus*.

SALSAPARILLIN, or **SALSEPARIN.** Syn. with SARSAPARILLIN.

SALSOLA. A genus of chenopodiaceous plants, growing on the seashore, and generally on soils rich in common salt. They yield a large quantity of ash, chiefly consisting of sodic carbonate, on which account several species (*Salsola Kali, S. Soda*, &c.) are cultivated for the preparation of natural soda, or barilla. *Salsola Soda* is cultivated for this purpose chiefly in Spain, near Alicante.

The ashes of several species of salsola from the Kirghis Steppe, have been analysed by Göbel (*Reise in die Steppen des südlichen Russlands*, Dorp. 1837 and 1838; *Handw. d. Chem.* vii. 204). The young plants of *Salsola brachiata*, air-dried, yielded 30 per cent. ash, of which 66·5 per cent. was soluble in water; older plants gave only 18 per cent. ash, containing 63·5 per cent. of soluble salts. Young plants of *S. clavata* gave 42 per cent. ash, of which 74 per cent. was soluble; young plants of *S. lanata* gave 19·0 per cent., of which 38 per cent. was soluble in water. Old plants of *S. laricina* gave 7·0 per cent. ash, containing 44·5 per cent. of soluble salts; old plants of *S. tamariscina* 9·3 per cent. ash, containing 45 per cent. soluble salts.

Composition of the Ash of various Species of Salsola.

	S. Kali.	*S. brachiata.*		*S. clavifolia.*		*S. lanata.*	*S. laricina.*	*S. tamariscina.*
		young	old	young	old			
Sulphate of Potassium . .	5·6	8·9	8·6	1·3	0·7	6·5	9·4	7·5
Carbonate „ . .	1·0	. .	. .	1·8				
Chloride „ . .	3·4	. .	. .	12·4	8·7	8·9	. .	0·2
Sulphate of Sodium . . .	. .	4·5	2·7	. .	. .	. .	7·1	
Chloride „ . . .	. .	14·8	19·4	. .	5·0	11·2	12·3	25·5
Carbonate „ . . .	31·1	26·2	24·1	43·8	46·0	4·2	6·9	8·1
Free Soda, with Sulphide and Hyposulphite of Sodium .	5·1	5·1	3·8	6·8	4·1	4·1	2·7	1·5
	49·2	59·5	58·6	66·1	64·5	34·9	38·4	42·8

SALT. Sodic chloride, *sea-salt*, or *common salt*, the substance which is always denoted when the word "salt" (Gr. ἅλς, Lat. *sal*, Fr. *sel*, Germ. *Salz*) is used without qualification in ordinary language, was doubtless the first body to which this name was given. The word salt itself, in its Greek form, sufficiently establishes this fact,—ἅλς in the feminine being used for the sea, and ἅλς in the masculine for the solid product left when sea-water evaporates. In endeavouring to trace some of the most important of the steps by which this word, from having been the specific name of a particular substance, has come to be used as a generic term of wider application than any other in the whole vocabulary of chemistry, we find that the first extension of its meaning was in connection with the leading idea which the etymology of the word shows to have been attached to it from the beginning. This idea evidently was very nearly what would have been expressed, in the language of a later time, by saying that sea-salt was the essence, or essential principle, of sea-water. Accordingly, when it was observed that other watery liquids yielded, under the same conditions as sea-water, a solid substance, not very unlike sea-salt in appearance, the name salt was applied to these substances also. Thus, according to Kopp (*Geschichte der Chemie*, iii. 2), Aristotle calls the residue deposited on cooling by the evaporated lixivium of wood-ashes, salt, and Dioscorides and Pliny enumerate as one of the kinds of salt, mild fixed alkali; some other allied substances also bore the same name. But, as Kopp very judiciously points out, this extension of the name salt to other bodies than that to which it was first applied, indicated ignorance of the real differences of these bodies, rather than any clear perception of analogies among substances recognised as distinct. The use of the term was, however, such as to show, clearly enough, that the notion which it originally conveyed was that of a soluble solid substance produced from a watery liquid by evaporation.

This original idea of solubility, as the most characteristic property of saline or salt-like substances, retained its ground down to the times of the alchemists; but, as the different bodies to which the common name of salt was applied came to be more accurately distinguished from each other, it became necessary to adopt for them distinctive appellations; and thus in the writings of Albertus Magnus, Raymund Lully, and their contemporaries of the thirteenth century, occur such specific names as *sal marinum*, *sal petræ* or *sal nitri*, *sal ammoniacum*, *sal vegetabile* (potashes), &c. All the substances denoted by these names have been ever since classed as salts: but that the ideas attached to the word salt, at the period referred to, were very vague and indefinite, is shown by the fact that all the then known metallic salts, a class of compounds which possess, in as marked a degree as any, the characters now recognised as saline, were denied the name of salts by Basil Valentine (in the latter part of the fifteenth century), and classed together as vitriols. There can be no doubt, however, that this arbitrary distinction, as it seems to us, between metallic salts and other salts, was in harmony with the chemical ideas generally prevailing at the time. For the alchemists, the main problem presented by chemistry was the study of the metals, just as for Lavoisier and his school it was combustion, and for Berzelius it was the quantitative composition of mineral salts as illustrating the doctrine of definite proportions. Hence it is not surprising that substances either produced from metals, or from which metals could be obtained, should have been regarded by the alchemists as of an essentially different nature, and, so to speak, as possessing a higher rank than the substances known to them as *salts*. Accordingly, this separation was generally maintained as long as alchemy held its ground, but was abandoned as wider views grew up in the science; and even during the alchemical period it was not recognised by those chemists who were not alchemists. Thus Bernard Palissy, in a tract, "*Des Sels divers et du Sel commun*" published in 1580, classed together as salts, common salt, saltpetre, the vitriols, alum, borax, sugar, corrosive sublimate, tartar, and sal-ammoniac. (See *Life of Bernard Palissy of Saintes*, by Henry Morley, London, 1855, pp. 96, 97.)

The most important modification which the original idea of a salt underwent, before the beginning of the eighteenth century, was that it implied a substance not only possessed of solubility, but capable of affecting the sense of taste. It is not clear at what period the latter property began to be generally recognised as an essential character of salts, but it was commonly received as such in the sixteenth century. In making the possession of taste an essential quality of salts, chemists were evidently led by the analogy of chloride of sodium, the original salt, whose remarkable flavouring power has been a chief cause of its common employment from the earliest ages. ("Can that which is unsavoury be eaten without salt?"—Job vi. 6.) During all this period, therefore, all that seems to have been implied, when this or that particular substance was called a salt, was that some undefined degree of resemblance in external qualities, especially in the two just mentioned, was perceived between it and common salt; and it is probable that the notion which underlay the application of the same name to these various compounds, was rather that of their being modifications of a single fundamental substance than radically distinct though analogous bodies.

But during the latter part of the fifteenth, the whole of the sixteenth, and a great part of the seventeenth centuries, the term salt was used not only in the sense that has been explained, as a generic name for certain definite preparable substances, but also in a much more abstract sense, as the name of one of the supposed ultimate elements of all material things.

Thus, according to Basil Valentine, all inorganic substances were made up of salt, sulphur, and mercury; and Paracelsus (in the early part of the sixteenth century) declared that the same three substances were the elements of all bodies, organic as well as inorganic—a doctrine which was adopted by a great many succeeding chemists. And until the rise of analytical chemistry, and the foundation of the modern views of the nature of the chemical elements by Boyle in the latter part of the seventeenth century, salt was almost always enumerated as one of the elements, although opinions varied considerably as to the others.

In order to understand this use of the word salt, it is needful to remember that the idea of an "element," at the period we are referring to, was very different from that which is expressed by the same word now. It had much less reference to *composition*, as now understood, than to what were supposed to be the intrinsic and fundamental *properties* of material bodies. The principles recognised as elementary by the chemists of that age, differed both in name and in attributes from the elements admitted by the Greeks; nevertheless, the notion of an element was still essentially of the same quality as that acted upon by Aristotle, when he selected as elements Fire, Water, Air, and Earth, on the ground that they appeared to him the most distinct embodiments of Heat and Cold, Dryness and Moisture, which he regarded as the fundamental qualities of matter. Accordingly, when we find salt spoken of as one of the elements, and as a constituent of all manner of substances—as it is, for instance, by Palissy in the treatise already referred to: "I tell you further, that there is nothing in this world which has no salt in it, whether it be in man, the beast, the trees, plants, or other vegetative things, or even in the very metals, &c."—we are not to understand the statement as we should if it were made by a modern chemist, but should rather take it as implying that saline properties (solubility and taste) were supposed to belong in some degree to all substances. In particular, the notion that salt was a constituent of the metals was clearly nothing more than the theoretical conception, in accordance with the general modes of thought prevailing at the time, which corresponded to the known fact that by various processes the metals could be actually transformed into salts; for the conversion, say, of iron into green vitriol, was not then regarded as a process of combination of iron with other substances, but simply as a process in which iron was modified in such a manner as to allow its previously latent saline qualities to be manifested.

The name salt being applied to all substances which were soluble and possessed of taste, included some which differed greatly in other properties. Thus, in addition to neutral salts, it included the acids and alkalis. As the properties of these two classes of bodies became known, it was gradually recognised that they were in many respects antagonistic, and especially that, by their action upon each other, their distinguishing characters were more or less completely obliterated, new and comparatively indifferent substances being generated. These observations led to the subdivision of salts into three classes, variously distinguished by different chemists. From about the year 1700, the names by which the three classes of salts were generally indicated were *salia acida*, *salia alcalina*, and *salia salsa*, *salia media*, or *salia neutra*.

The relation which had thus been already partially perceived between acids, alkalis, and neutral salts, was made by G. F. Rouelle, in 1744, the basis of a general theory of salts, which closely approximated to that very generally adopted in quite recent times. The importance of the step made by Rouelle was such as to make it desirable to state his views in his own words. In the introduction to a paper on Salts in the Memoirs of the Academy of Sciences of Paris, for the above-mentioned year (*Mém. Acad. Roy. Sciences*, 1744, p. 353), he says: "La plûpart des chymistes ne donnent le nom de sel neutre, moyen ou salé, qu'à un très-petit nombre de sels; il y en a même eu qui n'ont donné ce nom qu'au seul tartre vitriolé, demandant pour caractère de ces sels que l'acide et l'alcali qui les forment soient tellement unis qu'ils résistent à toute décomposition; d'autres ont admis avec le tartre vitriolé les deux sels neutres formés par l'union des acides du sel marin et du nitre à des bases alcali fixes, tels sont le sel marin et le nitre; d'autres y joignent trois autres sels formés par l'union des trois acides à un alcali volatil, qui sont le sel ammoniacal secret de Glauber ou le sel ammoniacal vitriolique, le sel ammoniacal ordinaire, et le sel ammoniacal nitreux; il y a eu d'autres chymistes qui ont joint au nombre de ces sels neutres plusieurs autres substances salines. Je donne à la famille des sels neutres toute l'extension qu'elle peut avoir; j'appelle sel neutre, moyen ou salé, tout sel formé par l'union de quelque acide que ce soit, ou minéral ou végétal, avec un alcali fixe, un alcali volatil, une terre absorbante, une substance métallique, ou une huile." And again, in another paper in 1754, he says, referring to the one already quoted: "J'ai étendu le nombre de ces sels autant qu'il était possible, en définissant génériquement le sel neutre un sel formé par l'union d'un acide avec une substance quelconque, qui lui sert de base et lui donne une forme concrète ou solide." (*Mém. Acad. Roy. Sciences*, 1754, pp. 573, 574: see also Kopp, *Geschichte der Chemie*, iii. 68, 69.) Rouelle was not the first to recognise that the combination of acids with alkalis gave rise to neutral salts; but, according to Kopp, he was the first to declare formation by the union of acid and base to be the characteristic mark of neutral salts, and thus rested the idea of a neutral salt upon chemical composition, instead of upon external properties.

As a consequence of the alteration which Rouelle introduced in the definition of salts, some substances which had previously been considered as belonging to it (for instance sugar) were excluded from it, and others—namely insoluble salts, such as horn-silver and calomel—which had previously been excluded, were now included in it; and, moreover, an essential distinction was made between acids and alkalis on the one hand, and neutral salts on the other. These views did not, however, immediately meet with universal acceptance. Solubility was still regarded by most chemists as an essential quality of salts. The idea which commonly prevailed as to the nature of salts, ninety or a hundred years ago, may be gathered from the following extracts. In the fourteenth volume, published in 1765, of Diderot and D'Alembert's "Encyclopédie," is an article on Salts, commencing thus: "SEL ET SELS.—On comprend sous le nom de *sel* trois espèces de substances; les acides, les alkalis, et les *sels* neutres; en réunissant les propriétés communes à ces trois classes, on trouve que les sels sont des corps solubles dans l'eau, incombustibles par eux-mêmes, et savoureux; il faut bien se défendre d'appeler *sel* tout ce qui se crystallise, sans quoi nous confondrions plusieurs corps très-différens entre eux." In a *Dictionnaire de Chymie* (Macquer's), published at Paris in 1766, salts are defined as follows:—"Les propriétés essentielles de toute matière qu'on doit regarder comme saline, sont d'affecter le sens du goût, ou d'avoir de la saveur, d'être dissoluble dans l'eau, et d'avoir toutes les autres qualités principales, comme la pesanteur, la fixité, moyennes entre celles de l'eau, et celles de la terre pure." (*Op. cit.* ii. 412). A few years later, Bergman, in his *Sciagraphia regni mineralis* (§ xx.), thus states the distinguishing marks of salts:—"Sales audiunt, qui in linguâ plus minus saporis excitant, et probe pulverati aquâ ebulliente, saltem millies ponderosiore, solvi possunt. Igne liquescunt et plerique mutantur vel destruuntur." In his *Thoughts on a Natural System of Fossils*, after characterising salts almost in the same words (§ xlvii.), he points out (§§ xlviii.—l.), that taste, depending on the varying perceptions of individuals, is necessarily a very uncertain criterion; while solubility, being a property which admits of an infinite number of degrees, is hardly less so, unless defined by arbitrarily-chosen conditions. Bergman seems, however, to have perceived that the saline character was fundamentally a matter of composition, even to the extent of inferring solubility in the case of substances which had not been proved experimentally to be soluble: thus, in § li. of the work last quoted, he says:—"Vitriolated ponderous earth, commonly called *spatum ponderosum*, aërated lime, fluorated lime, impregnated with the acid of the *lapis ponderosum*, are all saline earths by the force of composition, and are even without doubt soluble, though to what extent experience has not yet determined."

Such then were the prevalent opinions as to the nature of salts, when Lavoisier, by his discovery of the important functions of oxygen, changed the whole aspect of chemical science. Lavoisier's own ideas on the subject of salts are thus expressed by him:—"Les substances acidifiables, en se combinant avec l'oxygène, et en se convertissant en acides, acquièrent une grande tendance à la combinaison; elles deviennent susceptibles de s'unir avec des substances terreuses et métalliques, et c'est de cette réunion que résultent les sels neutres. Les acides peuvent donc être regardés comme de véritables principes salifians, et les substances auxquelles ils s'unissent pour former des sels neutres, comme des bases salifiables. . . .

"Cette manière d'envisager les acides ne me permet pas de les regarder comme des sels, quoiqu'ils aient quelques-unes de leurs propriétés principales, telle que la solubilité dans l'eau, etc. Les acides, comme je l'ai déjà fait observer, résultent d'un premier ordre de combinaisons; ils sont formés de la réunion de deux principes simples, ou au moins qui se comportent à la manière des principes simples, et ils sont par conséquent, pour me servir de l'expression de Stahl, dans l'ordre des mixtes. Les sels neutres, au contraire, sont d'un autre ordre de combinaisons, ils sont formés de la réunion de deux mixtes, et ils rentrent dans la classe des composés. Je ne rangerai pas non plus, par la même cause, les alkalis ni les substances terreuses, telles que la chaux la magnésie, etc., dans la classe des sels, et je ne désignerai par ce nom que des composés formés de la réunion d'une substance simple oxygénée avec une base quelconque." (*Traité élémentaire de Chimie*, ed. 1789, vol. i. pp. 162–164). Although these views were in the main, with the exception of what related to the constitution of the acids, only a reiteration of those expressed forty years previously by Rouelle, they were felt by Lavoisier to be so little in harmony with contemporary opinion, that he thought it needful to add to the passage we have quoted the following apologetic foot-note:—"On regardera peut-être comme un défaut de la méthode que j'ai adoptée, de m'avoir contraint à rejeter les alkalis de la classe des sels, et je conviens que c'est un reproche qu'on peut lui faire; mais cet inconvénient se trouve compensé par de si grands avantages, que je n'ai pas cru qu'il dut m'arrêter."

In accordance with these views, the history of whose spread and adoption makes part of that of the antiphlogistic system in general, a salt was a combination of a highly-oxidised substance (an acid) with a base. The bases of the metallic salts were already known to be oxides, and the same was soon demonstrated, by Davy, to be true of the earths, alkaline earths, and fixed alkalis. Hence salts soon came to be defined as compounds of electronegative oxides (acids), with electropositive oxides (bases), and all salts were consequently regarded as containing oxygen. Salts were, however, known in which the presence of oxygen could not be directly proved, and amongst them was common salt itself. As a natural consequence, the constitution of such bodies gave rise to much discussion. The application of Lavoisier's doctrine to the chlorides, for instance, caused them to be regarded as compounds of metallic oxides with muriatic acid, supposed to contain oxygen. This was the view adopted by Gay-Lussac and Thénard (*Mémoires d'Arcueil*, ii. 357, 358 [1809]; and *Recherches physico-chimiques*, ii. 155—176 [1811]) as the most probable conclusion that could be drawn from their investigations into the nature of these compounds, and maintained by Berzelius until about the year 1820. (See his *Lehrbuch der Chemie*, [first German edition, 1820, translated from the second Swedish edition], vol. i. especially, pp. 707—714; also *Jahresbericht*, i. 46, [1821]; ii. 60—62, 70 [1822]; iii. 98 [1823].) Davy, on the other hand, who never adopted very fully Lavoisier's views, regarded the chlorides as compounds of the metals with a simple body, chlorine, comparing them to the simple metallic oxides, and represented the salts known to contain oxygen as double oxides. Speaking of these substances, he says: "They are, in fact, all compounds of oxygen with double bases; and when one fixed alkali, or earth, or oxide, separates another, it may be supposed that the basis only is changed. Thus, where hydrat of potassa separates lime from its nitric solution, it may be conceived that the potassium only takes the place of the calcium, and that the oxygen and water of the hydrat of potassa unite to this metal, and that the potassium unites to the oxygene, nitrous acid and water of the solution." (*Elements of Chemical Philosophy* [1812], p. 495.)

The adoption of Davy's views of the constitution of the chlorides was greatly promoted by the discovery of iodine in 1811, and the investigation of it by himself and by Gay-Lussac in 1813—14, one of the first consequences of which was that Gay-Lussac himself became convinced of the elementary nature of both iodine and chlorine. And important additional evidence, that oxygen was not essential to the constitution of salts or acids, was afforded by Gay-Lussac's discovery of cyanogen, and analysis of anhydrous prussic acid, in 1815. In consequence of these discoveries, a large number of chemists, if they did not adopt Davy's views of the constitution of salts in general (for which see also the article ACIDS, i. 41, 42), at least admitted that, in addition to ordinary salts, which they regarded as formed by the union of (anhydrous) acids with metallic oxides, there was another class of salts—comprising the chlorides, iodides, sulphides, cyanides, and perhaps the fluorides—into whose composition oxygen did not enter. Berzelius, however, held fast to Lavoisier's definition of salts ("Unter Salz verstehen wir eine Verbindung einer Säure mit einem Alkali einer Erdart, oder einem Metalloxide:" *Lehrbuch*, ed. 1820, i. 817), and consistently declared in consequence that, if the chlorides, &c. were constituted as represented by the adherents of the new theory, they could not be salts at all. ("Daher ist das salzsaure Natron oder Kochsalz [welches durch seine Geschlechtsähnlichkeit mit anderen Salzen Anlass gegeben hat, das Wort Salz als allgemeine Benennung des ganzen Salzgeschlechts zu gebrauchen], der neuen Theorie gemäss, kein Salz mehr. . . . ."—*Op. cit.*—"Die salzsauren Salze sind in dieser Theorie keine Salze, z. B. Kochsalz ist nicht eine Verbindung von Natron mit einer Säure, sondern eine Verbindung von Natrium mit Chlor."—*Ibid.*) Berzelius perceived, what most chemists of that time do not seem to have done, that the chemical history of iodine afforded in reality no new argument in favour of Davy's theory, all the combinations of iodine admitting of precisely the same kind of interpretation as the corresponding compounds of chlorine, on the supposition that both were oxidised compounds of unknown elements. (For his views of the chlorine-compounds, see i. 902.) The sulphides he did not admit into the category of salts at all; the cyanides, however, especially cyanide of mercury and prussiate of potash, could not be denied the possession of distinctly saline properties. But even these substances were not regarded by him as affording conclusive evidence that true salts could exist without containing oxygen; for, although it was certain that they contained, in addition to metal, nothing but carbon and nitrogen, the latter element was at this time regarded by Berzelius as itself a compound of oxygen with an unknown radicle, nitricum. Representing one combining proportion of this supposed radicle by R (= 6), and one combining proportion of oxygen by O (= 8), his view of the constitution of nitrogen and its oxides may be represented by the following formulæ:—

Nitrogen	=	RO	Nitrous acid (anhydrous)	=	RO^4
Nitrous oxide	=	RO^2	Nitric peroxide	=	RO^5
Nitric oxide	=	RO^3	Nitric acid (anhydrous)	=	RO^6

(For the reasons urged by Berzelius in support of these views, which were mainly founded on the phenomena attending the formation of ammonium-amalgam, see his *Lehrbuch der Chemie*, ed. 1820, i. 225, 226; 491, 492; 613—619; 806; 810.)

The circumstance which chiefly contributed to make Berzelius at last receive the so-called "chloristic theory" was Faraday's discovery, in 1821, of the sesquichloride, protochloride, and bichloride of carbon. It had been, from the first, one of Davy's strongest arguments against the existence of oxygen in chlorine, and consequently in the chlorides, that chlorine was not decomposed by carbon even at the highest temperatures. The opponents of his views declared that this experiment was inconclusive, for chlorine could not be decomposed, under these circumstances, without the formation of carbonic acid or oxide, and (hypothetically) anhydrous muriatic acid, to the formation of which there would be no tendency unless these compounds were themselves capable of combining together, and they maintained that there was no evidence of the possibility of such a combination. The chlorides of carbon discovered by Faraday were, however, precisely such compounds; and, upon the old view of the constitution of chlorine, could not be otherwise represented than as combinations of (hypothetically) anhydrous muriatic acid, with anhydrous oxalic acid, carbonic oxide, and carbonic acid respectively. Such an interpretation of the nature of these substances seemed to Berzelius so little in harmony with their properties, as to be even less probable than the views as to the elementary character of chlorine and iodine, which he had hitherto opposed. He afterwards saw a confirmation of these views in the colour of red prussiate of potash, discovered in 1822 by Leopold Gmelin: in his account of this salt, in his Third Annual Report (p. 98), he says that he had hitherto regarded the reddish colour of the sesquichloride and other sesquisalts of iron as favouring the idea that they contained as a proximate constituent the red sesquioxide; but, as a red salt was now known which demonstrably contained no oxygen, he considered this view no longer tenable.

In 1825, Berzelius himself discovered the sulphur-salts, and thus afforded a fresh proof that substances perfectly devoid of oxygen could possess all the characters of salts. In consequence, he seems to have entirely changed his opinions as to what were the essential marks of a salt. He now says distinctly that it is not a question of composition but of properties: "When, for example, sodium combines with chlorine, the product is common salt, the most characteristic of all salts; but when sodium combines with oxygen, it does not produce a salt, but a substance which acquires properties analogous to those of common salt only by combination with an acid. The idea which is to be connected with the word salt cannot, therefore, be deduced from composition, for, in the first place, the salt is composed of two simple bodies, and in the second of two oxides. The idea of what a salt is must, consequently, be derived from that kind of electrochemical indifference, which chemists have from antiquity very fitly called *neutrality*, and which results from the combination of substances without respect to the elements of which the neutral compound is formed." (*Jahresb.* vi. 185 [1826].) Berzelius's views of the nature of salts are further illustrated by the manner in which he classified the simple bodies in relation to them. At the place last quoted he divides the elements as follows:—

A. Electronegative:

1. Those which produce *salts* by direct union with electropositive elements.—Halogens: namely, chlorine, iodine, and probably fluorine.
2. Those which produce *bases* by union with electropositive elements, and *acids* by union with electronegative elements of the third class.—Amphigens; namely, oxygen, sulphur, selenium, and tellurium.
3. The remaining non-metallic elements, and the electronegative metals: by union with the second class of electronegative elements they form *acids* (and sometimes also very weak bases). This class contains nitrogen, carbon, arsenic, &c.

B. Electropositive:

The electropositive elements do not admit of subdivision: by combination with electronegative elements of the first class, they form *salts*; with those of the second class, *bases*; with those of the third class, *alloys*.

Salts themselves were divided into two classes: the first class, called haloid salts, included those formed (like chloride of sodium) by the union of an electropositive metal with a halogen; the second class, amphid salts, was composed of those formed (like potassic sulphate) by the union of an acid and a base, and was subdivided into four genera—namely oxysalts, sulphosalts, seleniosalts, and tellurisalts—according to the nature of the amphigen contained in them. (See further Berzelius, *Jahresb.* viii. 137—143 [1828], where the same views are again insisted on.)

These views were accepted, almost without question, by the great majority of chemists; and they will be recognised by every reader as having been reproduced, with very little variation, in nearly every textbook of chemistry published from the year 1830 till within the last ten years, and even in many that are still more recent. It is hardly needful to say, that it is for this reason that we have discussed Berzelius's opinions at so great a length. There were, however, always a few chemists to whom the division into haloid salts and amphid salts appeared arbitrary and inadmissible. The most important of the earlier attempts to reduce all salts into a single class gave rise to the so-called "binary" theory, already alluded in the article ACIDS (i. 42 and 45, foot-note). This theory, however, never exerted a very important influence on the progress of chemistry, and it is therefore not needful to discuss the arguments by which it was supported and opposed.

If we try now to state what is the idea which is attached to the word salt, as at present used in chemical science, we find it impossible to do so in very precise terms. Probably we may most correctly define this idea by saying that it implies the capability of readily undergoing *double decomposition*. ("Nous appelerons *sels*, ou *corps binomes*, tous les composés chimiques formés par deux parties, l'une métallique et l'autre non-métallique, pouvant ainsi s'échanger par double décomposition."—Gerhardt, *Introduction à l'étude de la Chimie par le Système Unitaire*, 1848, p. 91.) In its most restricted signification, the word salt suggests a substance which, if soluble in water, can produce *rapid* double decompositions with other soluble substances, or, if insoluble, can be produced as a precipitate, as the result of a rapid double decomposition taking place between soluble substances. This is certainly the idea suggested by the application of the word salt to chloride of sodium, nitrate of potassium, sulphate of barium, nitrate of silver, hydrochlorate of aniline, &c. By an inevitable extension of meaning, the name salt is also sometimes given to substances which, like chloride of ethyl, give rise to *slow* processes of double decomposition with aqueous solutions of the salts specially so called. By a still further extension, it is sometimes applied to such bodies as acetate of ethyl, or stearin, and even these compounds do not mark the limit of its occasional application. The fact is, that as there is no class of bodies known—not even excepting the elements themselves—which do not, under certain conditions, give rise to reactions which must (or may) be represented as double decompositions, so there is no class of bodies to which the name salt, as implying capability of double decomposition, is completely inapplicable. The name is, however, most commonly and most appropriately applied to those bodies of which reaction by double decomposition is the most characteristic property, and which exhibit such reactions under the most familiar conditions. G. C. F.

SALT GARDENS. *Marais salins.* Shallow ponds or ditches, excavated on the seashore and puddled with clay, for concentrating sea-water by spontaneous evaporation, and obtaining common salt. (See SODIUM, CHLORIDE OF.)

SALT LAKES. *Salzseen.* Inland seas containing considerable quantities of chloride of sodium, and other constituents of sea-water and salt-springs, carried down by the various streams which flow into them. As the water evaporates during the hotter season of the year, chloride of sodium, more or less pure, separates out, and the remaining water approaches in composition to the mother-liquor of ordinary salt-springs, containing considerable quantities of the chlorides of magnesium and calcium, and comparatively little chloride of sodium; also bromides, potassium-salts, &c. The proportions of these several constituents vary with the season of the year, according to the temperature, and the quantity of fresh water brought down by rivers.

Salt-lakes are especially numerous in the great basin of Northern Asia, the lowest part of which is occupied by the Caspian Sea and Lake Aral. In the government of Astrachan there are 129 of these lakes, of which 32 are worked for the production of salt. Near Kistiar, in the government of the Caucasus, there are 21, from 18 of which salt is likewise obtained. One of the most considerable of these salt-lakes is the Elton Lake, in the Steppe of Kirghis, between the Rivers Volga and Ural. As the water of this lake evaporates in summer, the chloride of sodium separates out in loose masses, which afterwards become denser. It is very impure, containing large quantities of magnesium-chloride, which gives it a sharp and bitter taste. If, however, this deposited salt remains in the lake, and is exposed to the solvent action of fresh water in the following spring, the chloride of magnesium and other foreign salts, being more soluble than the chloride of sodium, are first dissolved, and the chloride of sodium remains as a compact, stony, bluish mass, having a pure saline taste. A black mud is at the same time deposited upon it, and forms a sharp demarcation between the deposits of successive years. This lake, in 1832, yielded, 40,000 tons of salt.

The following tables exhibit the percentage composition of the water of several salt-lakes :—

Water of the Dead Sea.

	C. G. Gmelin.	Marchand.	Booth and Muckle.	Moldenhauer.	Boussingault.
		Sp. gr. 1·185	Sp. gr. 1·227	Sp. gr. 1·160 (summer of 1854).	Sp. gr. 1·194 (spring of 1865).
Chloride of sodium . . .	7·1	6·5	7·8	2·9	6·5
Chloride of magnesium . .	11·8	10·5	14·6	6·8	10·7
Chloride of calcium . . .	3·2	2·9	3·1	1·5	3·6
Chloride of potassium . .	1·7	1·4	0·6	2·4	1·6
Chloride of manganese . .	0·2				
Chloride of aluminium . .	0·1	0·01	. .	. .	trace
Bromide of magnesium . .	0·4	0·2	. .	0·2	0·5
Bromide of potassium . .	. .	. .	0.03		
Sulphate of calcium . . .	0·05	0·08	0.07	0·06	0·04
Water	74·5	78·2	73·6	86·1	77·2

The following analyses of the water of the Dead Sea, in different parts and at different depths, have lately been published by A. Terreil (Compt. rend. lxii. 1329; Zeitschr. f. Chem. [2] ii. 415):—

Dead Sea.

	In the sea near Ras Dale.	Lagune north of Sodom.	North side near the island.	Five miles east of Wady Mrabba.	Near Ras Mersed.	Five miles east of Ras Feschkah.	The same.	Five miles east of Wady Mrabba.
Depth in metres . . .	Surface	Surface	Surface	20	42	120	200	300
Specific gravity at 15° . .	1·0216	1·0375	1·1647	1·1877	1·2151	1·226	1·2300	1·2563
Solid residue in 100 pts. water .	2·7078	4·7683	20·5789	20·4311	26·0994	26·2648	27·1606	27·8135
Chlorine	1·7628	2·9826	12·6521	14·5543	16·5443	16·6340	17·0423	17·4985
Bromine	0·0167	0·0835	0·4568	0·3240	0·4834	0·4870	0·4385	0·7093
SO^3[? SO^4]	0·0202	0·0676	0·0494	0·0362	0·0447	0·0451	0·0459	0·0523
Magnesium	0·4197	0·3470	2·5529	2·9881	4·1004	4·1306	4·2006	4·1428
Calcium	0·2150	0·4481	0·9094	1·1472	0·3693	0·3704	0·4218	1·7269
Sodium	0·0885	0·7845	2·2400	1·3113	2·4786	2·5071	2·5107	1·4300
Potassium	0·0474	0·0779	0·3547	0·3520	0·2421	0·3990	0·4503	0·4386
	2·5703	4·7912	19·2153	20·7131	24·2628	24·5732	25·1101	25·9984

Traces of carbonic acid, ammonia, ferric oxide, alumina, and organic matter were likewise found; no iodine, phosphoric acid, lithium, cæsium, or rubidium.

The table shows:—1. That the density and concentration of the water increases with the depth.—2. That the composition varies throughout the entire breadth. The water to the north of Sodom contains a larger proportion of sodium- than of magnesium-chloride; and, as a consequence of this, small fish are able to live in it.—3. That the proportions of the different constituents are the same at all depths, the bromine alone appearing to increase in a greater ratio at a depth of 300 metres.

The quantities of potassium-salt and of bromine in the water are remarkably great. The water of the springs and rivers in the neighbourhood contains chlorine, sulphuric acid, carbonic acid, lime, magnesia, potash, and soda, but no appreciable quantity of bromine.

Salt Lakes of the Northern Asiatic Basin.—*a.* Oroomiah Lake, in the north-west of Persia; specific gravity 1·555 (Hitchcock).—*b.* Elton Lake, in spring (Göbel).—*c.* The same in summer (Erdmann).—*d.* The same in autumn (G. Rose). In the clay soil of the shore of this lake, Rose found small crystals of gypsum; small groups of crystals of magnesium-sulphate were also found floating on the water.—*e.* Bitter-salt Lake of Kigatsch, one of the arms by which the Volga flows into the Caspian Sea. At the bottom of this lake there is a deposit of sodio-magnesic sulphate, a foot thick.—*f.* Salt-lake of Tasly, near the highroad from Sympheropol to Eupatoria.—*g.* Lake of Bogdo, north-east of the Bogdoberg in the Caspian Steppe.—*h.* Salt-lake of Tschakrakskoi, not far from Kertsch, separated only by a narrow strip of land from the Sea of Azof.—*i.* Stepanow Lake.—*k.* Indertsch Lake.—*l.* Putrid lake on the east coast of the Crimea, separated only by a narrow tongue of land from the Sea of Azof. The water contains a small quantity of calcic sulphate, and smells of sulphydric and hydrochloric acids.—*m.* Salt-lake of Arsargar, the largest next to the Bogdo Lake, between the Rivers Volga and Ural.

100 pts. of the Lake-water contain:—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*k.*	*l.*	*m.*
Chloride of sodium .	19·0	13·1	7·4	3·8	10·5	18·1	21·6	28·9	22·4	23·9	14·2	17·8
„ magnesium	0·5	10·5	16·3	19·7	9·9	5·7	4·9	4·2	0·9	1·7	1·9	0·2
„ calcium .	. .	. .	. .	. .	. .	. .	0·9					
„ potassium	. .	0·2	. .	0·2	. .	0·6	. .	. .	. .	0·1		
Sulphate of potassium	0·1	. .	0·04	. .	. .	0·3	0·1	. .	0·05	0·04	. .	0·08
„ magnesium	0·8	1·6	2·2	5·3	8·2	2·3	1·0	4·2	0·7	0·3	1·2	0·04
Water	79·5	74·4	73·5	70·8	71·3	72·9	71·5	73·5	75·9	73·8	82·6	81·9
	99·9	99·8	99·44	99·8	99·7	99·9	100·0	110·8	99·95	99·84	99·9	100·02

The analyses *e* to *m* are by Göbel (*Reise in die Steppen des südlichen Russlands*): these waters were examined for bromides and potassium-salts only in a few cases; but it is probable that these salts exist in all salt-lakes. (*Handw. d. Chem.* vii. 218.)

SALTPETRE. Nitrate of potassium (see Nitrates, iv. 98). Nitrate of sodium is often called Chili Saltpetre.

SALT-RADICLE. The chlorous or electronegative constituent of a salt, according to the binary theory: *e.g.*, Cl in KCl, SO^4 in K^2SO^4, &c.

SALTS, NOMENCLATURE OF. See Nomenclature (iv. 125).—The following salts were denoted in the older language of chemistry by particular names, some of which are still occasionally used:—

Salt (Ammoniacal, Fixed). Chloride of calcium.

Salt (Ammoniacal, Secret) of Glauber. Sulphate of ammonium.

Salt (Arsenical, Neutral) of Macquer. Acid arsenate of potassium.

Salt (Bitter, Cathartic). Sulphate of magnesium.

Salt (Common). Chloride of sodium.

Salt (Digestive) of Sylvius. Acetate of potassium.

Salt (Diuretic). Acetate of potassium.

Salt (Epsom). Sulphate of magnesium.

Salt (Febrifuge) of Sylvius. Chloride of potassium.

Salt (Fusible). Phosphate of ammonium.

Salt (Fusible) of Urine. Phosphate of sodium and ammonium.

Salt (Glauber's). Sulphate of sodium.

Salt (Green). In the mines of Wieliczka the workmen give this name to the upper stratum of native salt, which is rendered impure by a mixture of clay.

Salt (Marine). Chloride of sodium.

Salt (Marine, Argillaceous). Chloride of aluminium.

Salt (Microcosmic). Phosphate of sodium and ammonium.

Salt (Nitrous Ammoniacal). Nitrate of ammonium.

Salt of Amber. Succinic acid.

Salt of Benzoin. Benzoic acid.

Salt of Canal. Sulphate of magnesium.

Salt of Colcothar. Sulphate of iron.

Salt of Egra. Sulphate of magnesium.

Salt of Lemons (Essential). Acid oxalate of potassium.

Salt of Saturn. Acetate of lead.

Salt of Sedlitz. Sulphate of magnesium.

Salt of Seignette. Tartrate of potassium and sodium.

Salt of Soda. Carbonate of sodium.

Salt of Sorrel. Acid oxalate of potassium.

Salt of Tartar. Carbonate of potassium.

Salt of Vitriol. Purified sulphate of zinc.

Salt of Wisdom. Ammonio-mercuric chloride, $2NH^4Cl.Hg''Cl^2.H^2O$.

Salt (Perlate). Disodic orthophosphate.

Salt (Polychrest) of Glaser. Sulphate of potassium.

Salt (Sedative). Boracic acid.

Salt (Spirit of). Hydrochloric acid was formerly called by this name, which it still retains in commerce.

Salt (Sulphureous) of Stahl. Sulphite of potassium.

Salt (Wonderful). Sulphate of sodium.

Salt (Wonderful, Perlate). Disodic orthophosphate.

SALT SPRINGS. This name is applied to waters which contain large quantities of chloride of sodium in proportion to their other constituents, and are therefore used for the extraction of that salt. In many saltworks, artificial salt-springs are formed by dissolving rock-salt or bay-salt in sea-water, or in a weak solution of sodium-chloride. (See Sodium, Chloride of.)

SALVIA. The garden sage, *Salvia officinalis*, yields, by distillation with water, an essential oil, which is light-yellow or nearly colourless when fresh, but after a time becomes darker and deposits a camphor. It has an aromatic taste, and a penetrating camphoraceous odour, like that of the plant. It floats on water, its specific gravity varying from 0·86 to 0·92 (Zeller). It boils between 130° and 160°, but not at a constant temperature. According to Rochleder (Ann. Ch. Pharm. xliv. 4), the composition and boiling-point of the oil vary greatly with its age, and when rectified over solid potash, it yields oils differing in composition and boiling-point. These oils may be regarded as compounds of the hydrocarbon C^6H^{10}, with varying quantities of oxygen (from 3 to 11 per cent.). Sage-oil treated with cold concentrated nitric acid becomes hot, and is converted, with evolution of gas, into a red resinous mass, which when distilled with water gives off common camphor, $C^{10}H^{16}O$, mixed with an oil. When sage-oil is dropped into fuming nitric acid at the boiling heat, it dissolves, giving off a mixture of carbonic anhydride and nitric oxide. If the liquid be then distilled with water, pure camphor collects in the condensing tube. In the formation of camphor from sage-oil, 2 atoms of the hydrocarbon, C^6H^{10}, give up 2 at. C and 4 at. H, which escape as carbonic anhydride and water:

$$2C^6H^{10} + O^7 = C^{10}H^{16}O + 2CO^2 + 2H^2O.$$

Another camphor, or stearoptene, is deposited from sage-oil when kept for a long time in a badly-closed vessel. (Herberger, Repert. Pharm. xxxiv. 138.—Gm. xiv. 399.)

Hlasiwetz (J. pr. Chem. li. 355), by boiling volatile oil of mustard with soda-lime, once obtained an oil which had the odour of sage-oil, and contained 80·0 per cent. carbon, 11·1 hydrogen, and 8·9 oxygen, agreeing nearly with the formula $C^{12}H^{20}O$ (80·25 C, 10·91 H, and 8·84 O). Its formation may perhaps be represented by the equation:

$$\underset{\text{Allylic sulphocyanate.}}{5(C^3H^5.CyS)} + 3Na^2O = \underset{\text{Sage-oil.}}{C^{12}H^{20}O} + \underset{\text{Sodic propionate.}}{C^3H^5NaO^2} + \underset{\text{Sodic sulphocyanate.}}{5NaCyS.}$$

Respecting the ferment-oil of *Salvia pratensis*, see ii. 636.

SALYLIC ACID. This name was given by Kolbe and Lautemann to a supposed isomer of benzoic acid. Chiozza, as already observed (p. 154), by treating the product of the action of phosphoric chloride on salicylic acid with water, obtained an acid having the composition of chlorobenzoic acid, $C^7H^5ClO^2$. This acid was afterwards examined by Limpricht and v. Uslar, who found that it differed in crystalline form and melting-point from ordinary chlorobenzoic acid (i. 555), and therefore regarded it as isomeric with the the latter. This conclusion was corroborated by the experiments of Kolbe and Lautemann (p. 154), who designated the chlorinated acid obtained from salicylic acid, as chlorosalylic acid; also by those of Kekulé (Ann. Ch. Pharm. cxvii. 145; Jahresb. 1860, p. 395). Kolbe and Lautemann also found that chlorosalylic acid differed from chlorobenzoic acid in its behaviour with sodium-amalgam, the latter being scarcely acted upon thereby, whereas the former is easily deprived of the whole of chlorine, and is converted into salylic acid, $C^7H^6O^2$, isomeric with benzoic acid.

Salylic acid precipitated from the alkaline solution by hydrochloric acid, and purified by recrystallisation from water, is said to form very small needles, which under the microscope never exhibit the indented form of benzoic acid. It is more volatile than the latter, melts at nearly the same temperature, viz. at 119° (benzoic acid melting at 121°), is much more soluble than benzoic acid, 1 pt. of it dissolving at 0° in 237 pts. water, whereas benzoic acid requires 607 pts. Some of the salts of salylic acid differ also in form and solubility from the corresponding benzoates. (Kolbe and Lautemann.)

Griess, by acting on diazobenzo-oxybenzamic acid (iv. 293) with nitrous acid, has also obtained an acid isomeric with benzoic acid, which he regards as identical with Kolbe and Lautemann's salylic acid.

On the other hand, according to E. Reichenbach and Beilstein (Ann. Ch. Pharm. cxxxii. 309; Bull. Soc. Chim. 1865, ii. 53), the so-called salylic acid, whether prepared from salicylic or from diazobenzo-oxybenzamic acid, is nothing but ordinary benzoic acid, more or less contaminated with foreign substances. After being distilled with water, converted into a sodium-salt, precipitated by hydrochloric acid, and once recrystallised, it exhibits all the characters of pure benzoic acid; likewise in its salts, and in the nitro-acid prepared from it.

Gräbe (Ann. Ch. Pharm. cxxxvi. 124; Bull. Soc. Chim. 1866, i. 432), by treating methylic methylsalicylate, $C^7H^4(C^2H^3)^2O^3$ (p. 162), with potash, has obtained an acid containing $C^8H^8O^3$, which he regards as methoxysalylic acid, $C^7H^5(CH^3)O^3$, perhaps methoxybenzoic acid. [Cahours obtained salicylic acid by the same reaction].

This acid crystallises in large tables, slightly soluble in cold water, easily soluble in boiling water and in ether. Its solution is strongly acid, and does not give with ferric salts the reaction characteristic of salicylic acid. It melts at 99°, and is partly resolved by distillation into carbonic anhydride and anisol.

Ethylic methylsalicylate treated with potash yields, in like manner, an acid containing $C^9H^{10}O^3 = C^7H^5(C^2H^5)O^3$. (Gräbe.)

SAMADERA INDICA (Gärtn.), *Vithmannia elliptica* (Vahl). A tree of the simarubaceous order (class *Terebinthaceæ*), growing in Java, and called by the Malays *Galip Pahit*. The almond-shaped fruits (which are enclosed in leathery capsules) and the bark are distinguished by a peculiar intensely bitter taste. According to C. L. Blume (Arch. Pharm. cxlvi. 265; Handw. vii. 222), the fruit and bark contain, in 100 pts.:—

	Fruit.	Bark.
Matters soluble in ether . . .	34·2	1·4
" " alcohol . . .	8·4	5·1
" " water . . .	10·6	1·2
" " potash . . .	0·1	trace
Cellulose	39·0	70·6
Water . . . , . . .	4·6	11·8
Ash-constituents	2·7	7·9

Ether extracts from the fruit, a colourless oil, having a peculiar odour, and saponifiable by alkalis. The alcoholic extract of the fruit consists chiefly of a brown, very bitter substance (perhaps a resin), which is somewhat soluble in water, absorbs moisture from the air, and deliquesces.—The aqueous infusion of the fruit yields a deliquescent, very bitter extract, containing tannic acid and a peculiar bitter principle called samaderin. The ash of the fruit contains carbonate of calcium and the chlorides of calcium and potassium.

From the bark, ether extracts a light-yellow fat of soft resinous consistence, which is only partially saponified by alkalis, and appears to be a mixture of resin and fat. The alcoholic and aqueous extracts of the bark have the same constituents and properties as those of the fruit.

Samaderin, the chief bitter constituent of the bark and fruit, is most easily prepared from the aqueous infusion by evaporating it to an extract, and treating the extract repeatedly with small quantities of alcohol; it may be purified by solution in water, and treatment with animal charcoal. It is dazzling white, with a foliated and somewhat feathery crystalline structure; has a persistent and intensely bitter taste, stronger perhaps than that of any other known substance; dissolves in water more easily than in alcohol, and to a slight extent also in common ether. Its solutions are perfectly neutral. When heated, it melts and gives off vapours having a sharp bitter taste. Hydrochloric and nitric acids colour it yellow. Strong sulphuric acid immediately produces with it a splendid red-violet colour, which disappears after a while; a considerable quantity of feathery, strongly iridescent crystals is formed at the same time. Samaderin produces no particular reaction with metallic salts, or with tincture of iodine, chromate of potassium, or ferrocyanide of potassium.

SAMARSKITE. Uranoniobate of yttrium and iron, occurring near Minsk, in the Ilmen Mountains (iv. 55).*

SAMBUCUS. A genus of plants belonging to the order *Caprifoliaceæ*. The berries of the dwarf elder or danewort (*Sambucus Ebulus*) contain malic acid (Braconnot), and a very gelatinous soft resin which may be used as birdlime.

The root-bark of the common elder (*Sambucus nigra*) contains, according to Simon, an emetic and purgative soft resin, which may be obtained by treating the alcoholic extract with ether, and evaporating.—The flowers contain a volatile oil, which is very soluble in water, and is therefore not easily obtained by distillation with water. The best way of preparing it, according to Winckler, is to concentrate the water in which fresh elder-flowers have been macerated, saturate it with common salt, shake up with ether, and evaporate the ether. It is colourless, lighter than water, and has the penetrating odour of the flowers, which, like musk, is capable of filling a very large space. At 0° it solidifies to a crystalline mass, like oil of roses. It has a very high boiling-point. When exposed to the air, it turns brown, thickens, and acquires the odour of decayed elder-flowers. It is said to contain sulphur. Elder-berries contain, according to Scheele, malic but no citric acid; also sugar, gum, a peculiar sudorific substance (which likewise exists in the flowers), and a red colouring matter, which is turned blue by a small quantity of alkali, green by a larger quantity.

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* It is there called "uranoniobite" of yttrium, &c.; but the acid formerly called niobine, or hyponiobic acid, is now known to be the only oxygen-acid of niobium, and is therefore called *niobic acid* (iv. 785).

SAMECH PARACELSI. An obsolete name of neutral potassic tartrate.

SAMOÏTE. An aluminous silicate allied to allophane, occurring in stalactitic forms in the lava of Upolu, an island of the Navigator group. It has a lamellar structure, whitish colour, and slightly nacreous lustre; hardness = 4·0 to 4·5; specific gravity = 1·7 to 1·9. Contains, according to B. Silliman, jun., 31·26 per cent. silica, 37·21 alumina, and 30·45 water, together with 4·06 magnesia, 0·01 calcic carbonate, 0·06 soda; according to another analysis, however, 35·19 silica, 31·95 alumina, and 30·80 water; the formula is therefore doubtful.

SAMPHAN. Syn. with Sapan.

SAND. This name is mostly applied to quartz occurring in a granular or pulverulent form, as on the seashore, in the beds of rivers, and covering extensive tracts on many parts of the earth's surface; but it is also extended to other minerals occurring in a similar condition: hence the terms dolomitic sand, iron sand, titaniferous sand, &c.

SANDAL-WOOD. *Sandal-wood, Santal-wood, Red Saunders-wood.*—A dye-wood furnished by the *Pterocarpus Santalinus*, a papilionaceous tree indigenous in the tropical parts of Asia. It occurs in commerce, sometimes in large heavy billets of a fine red colour (caliatur-wood)—sometimes as a red, loose, dusty powder. It has a somewhat harsh taste, and when warmed or rubbed gives off a faint agreeable odour. It is used in India, together with one-tenth of sapan-wood, chiefly for dyeing silk and cotton, to which, and also to wool, it imparts reds of various shades, according to the kind of mordant used. (See *Ure's Dictionary of Arts*, &c., iii. 631.)

Sandal-wood contains a peculiar red resinous colouring-matter, called **santalin**, and, according to **Meier** (Ann. Ch. Pharm. lxxii. 320), five other amorphous resinous bodies which he designates as **santalic oxide**, **santalide**, **santaloïde**, **santalidide**, and **santaloïdide**; the last four being extracted from the wood by water—the first, together with santalin, by alcohol. These five bodies have not, however, been obtained pure, and their separate existence is very doubtful.

Santalin, or **santalic acid**, $C^{15}H^{14}O^{5}$ (?), is prepared by treating the wood with ether, and evaporating the resulting solution; dissolving the highly-coloured crystals thus obtained in alcohol, after having exhausted them with water; precipitating the alcoholic solution with acetate of lead; boiling the violet precipitate several times with alcohol, then suspending it in that liquid, and decomposing it with dilute sulphuric acid. (**Meier**.)

Santalin forms small crystals of a fine red colour, and without taste or smell. It is insoluble in water, but very soluble in alcohol, forming a blood-red solution which reddens litmus. It melts at 104°, and at a higher temperature becomes resinous and puffs up. It contains, according to **Westermann** and **Häffely** (Ann. Ch. Pharm. lxxiv. 226), 65·85 per cent. C and 5·2 H, the formula $C^{15}H^{14}O^{5}$ requiring 65·7 C, 5·1 H, and 29·2 O.

The alcoholic solution of santalin precipitates lead-salts, but not the salts of barium, silver, or copper. Santalin dissolves easily in ammonia and in potash, forming violet solutions, which precipitate the alkaline earths.

The *barium-salt* is a violet crystalline precipitate, which, when dried at 100°, gives by analysis 53·2 to 53·7 per cent. C, 4·6 to 3·5 H, and 22·9 BaO, the formula $C^{30}H^{26}Ba''O^{10}$ requiring 52·7 C, 3·8 H, and 22·4 BaO.

The *lead-salt*, $C^{30}H^{26}Pb''O^{10}.Pb''H^{2}O^{2}$, gave by analysis 35·3 to 37 per cent. C, 2.8 H, and 44·6 to 44·9 lead-oxide, the formula requiring 36·2 C, 2·8 H, and 44·5 PbO.

SANDARACA. Syn. with Realgar (i. 386).

SANDARACH. A gum-resin which exudes from *Thuja articulata*, a small coniferous tree growing in Barbary. It occurs in pale-yellow elongated plates, covered with a very fine dust, and having a vitreous lustre on the fractured surface. It has a faint odour, and crumbles between the teeth without softening. According to **Johnston** (J. pr. Chem. xvii. 157), sandarach is a mixture of three acid resins. The α-resin forms a white or yellow powder, slightly soluble in alcohol, and not easily fusible. It forms but a small part of the entire resin, and contains 78·04 to 78·46 per cent C, and 9·80 to 9·91 H, whence Johnston deduces the formula $C^{20}H^{30}O^{2}$ (calc. 79·47 C, 9·93 H, and 10·60 O). The β-resin, which forms three-fourths of the whole, has a light-yellow colour, softens at 100°, and dissolves easily in cold alcohol. Contains 75·08 to 76·60 C, and 9·71 to 10·04 H, whence $C^{20}H^{30}O^{3}$ (calc. 75·47 C, 9·41 H, and 15·12 O). The γ-resin is a light-yellow powder, soluble in boiling alcohol, melting with difficulty, and decomposing at the same time. Contains 75·53 to 75·59 C, and 9·35 to 9·47 H, whence the formula $C^{20}H^{30}O^{3}$.

SANDEL-WOOD. Syn. with Sandal-wood.

SANGUINARIA CANADENSIS. The root of this plant, belonging to the papaveraceous order, contains sanguinarine or chelerythrine, and, according to Gibb (Pharm. J. Trans. [2] i. 454), two other alkaloids, called porphyroxine and puccine; but the two latter have been but imperfectly examined. (Gm. xvii. 162.)

SANGUINARINE. *Chelerythrine, Pyrrhopine.* $C^{19}H^{17}NO^4$. (Dana, Annals of the Lyceum of New York, ii. 245.—Probst, Ann. Ch. Pharm. xxix. 120; xxxi. 350.—Polex, N. Br. Arch. xvi. 77.—J. Schiel, Ann. Ch. Pharm. xliii. 233; Sill. Am. J. [2] x. 220.—Gm. xvii. 156.)—An alkaloïd discovered, as sanguinarine, by Dana, in the roots of *Sanguinaria canadensis*; as chelerythrine, by Probst, and as porphyroxine by Polex, in the common celandine (*Chelidonium majus*): the identity of the alkaloïds from these two sources was demonstrated by Probst and Schiel. In celandine it is found chiefly in the roots and unripe fruit; in *Sanguinaria* it exists also in the leaves, and most probably in the seed. It is also found in the roots of the yellow-horned poppy (*Glaucium luteum*), together with glaucopicrine, but not in the green parts of the plant, which contain glaucine (ii. 845, 846).

Preparation: 1. From the roots of *Sanguinaria canadensis.*—The dried and powdered root is exhausted with ether, hydrochloric acid gas is passed into the filtrate, and the impure hydrochlorate o fsanguinarine thereby thrown down, is collected and dried. In the ether there remains a brown greasy resin, together with a little sanguinarine, which is recovered by evaporating, exhausting the residue with water containing sulphuric acid, and precipitating by ammonia. The precipitated hydrochlorate is dissolved in water; the solution is precipitated by ammonia; the precipitate is washed, dried, and dissolved in ether; and the solution is shaken with animal charcoal till the supernatant liquid appears colourless. The precipitate, again thrown down from the filtrate by hydrochloric acid gas, is decomposed by aqueous ammonia, and afterwards washed and dried (Probst; Schiel). Schiel purifies sanguinarine extracted by other methods, by precipitating its ethereal solution with hydrochloric acid gas or sulphuric acid.

2. From the roots of *Chelidonium majus.*—The fresh or dried root is exhausted with water containing sulphuric acid: the liquid is precipitated by ammonia; and the precipitate is washed, freed from water as far as possible by pressing, and dissolved, while still moist, in alcohol containing sulphuric acid. The alcoholic solution, diluted with water, is submitted to distillation, and after the alcohol is driven off, precipitated by ammonia. The precipitate is dried between bibulous paper as quickly as possible, at a very gentle heat, powdered, and treated with ether, which dissolves chiefly sanguinarine. On expelling the ether, there remains a viscid turpentine-like mass, to be treated with as small a quantity as possible of water containing hydrochloric acid, which leaves resin undissolved. The solution is evaporated to dryness, and the residue washed with ether, hydrochlorate of sanguinarine then remaining. This is dissolved in a little cold water, which leaves most of the hydrochlorate of chelidonine undissolved; the solution is evaporated, and the residue again treated with water so long as hydrochlorate of chelidonine continues to separate. From the last aqueous solution the sanguinarine is thrown down by ammonia, and is purified by washing and drying, and subsequently dissolving in ether and evaporating. (Probst.)

3. From *Glaucium luteum.*—The dried and powdered roots of plants of one to two years' growth are exhausted with water containing acetic acid; the extract is precipitated by excess of ammonia; and the precipitate is washed, dried, and exhausted with ether, which leaves nearly pure sanguinarine on evaporation. The product is dissolved in the smallest possible quantity of water acidulated with hydrochloric acid; the water and excess of acid are evaporated; and the remaining hydrochlorate of sanguinarine is freed from chlorophyll by washing with ether, after which it is dissolved in a little water, and mixed with an equal volume of strong hydrochloric acid, which precipitates it almost completely, the supernatant liquid retaining only a small quantity, precipitable by ammonia. The precipitated salt may be obtained in the crystalline form, by dissolving it in water and evaporating the solution. By decomposition with ammonia it yields sanguinarine, which is crystallised from ether, with addition of water. (Probst.)

Properties.—Sanguinarine is obtained from absolute alcohol, by spontaneous evaporation, in groups of crystalline nodules (Probst); in white, pearly, fine grains (Dana); in star-shaped groups of transparent needles, and white nodules (Polex). It is insoluble in water, but soluble in *alcohol* and *ether*. The ethereal solution leaves, on evaporation, a turpentine-like body, which gradually hardens to a shining friable mass (Probst). The crystals become opaque and brown on drying (Polex). It is tasteless (Schiel); in the mouth it slowly creates a very faint taste (Dana); in alcoholic solution it has a burning sharp taste (Probst); very bitter (Schiel). It acts as a powerful narcotic poison. The dust excites violent sneezing (Probst). According to Dana and Schiel, it has an alkaline reaction; but according to Probst and Polex, it is neutral. On exposure to the air it gradually assumes a yellowish-white colour (Dana), and in presence of small quantities of acid vapours becomes immediately red (Polex; Schiel). It softens at 65° like a resin (Probst), melts at a somewhat high temperature, and burns completely, giving off ammoniacal vapours (Polex). It is decomposed by nitric acid. Its composition (at 100°—105°) is shown in the following table:—

	Calculation.		Schiel. *a.*	Schiel. *b.*
C^{19}	228	70·59	69·66	70·34
H^{17}	17	5·26	5·16	5.21
N	14	4·33	5·23	5·07
O^4	64	19·82	19·95	19·38
$C^{19}H^{17}NO^4$	323	100·00	100·00	100·00

a was prepared from *Sanguinaria*, *b* from *Chelidonium*.

Sanguinarine unites with *acids*, which it colours a fine orange-red, forming neutral salts, partly crystallisable, having a burning sharp taste, a narcotic action, and dissolving, for the most part, in water. From the solutions, sanguinarine is separated by ammonia, the fixed alkalis, or magnesia, in the form of a grey-white curdy precipitate (Probst). Concentrated acids have but little action on sanguinarine in the cold (Polex). Acetate of sanguinarine forms yellowish-white precipitates with tartar-emetic, ferric chloride, mercurous nitrate, mercuric chloride, and silver nitrate: iodine precipitates the solution of a crimson, chromate of potassium of a yellow, and chloride of gold of a dark-red-yellow colour. Basic acetate of lead and tincture of galls do not produce precipitates. (Polex.)

SANGUISORBA PRÆCOX. A rosaceous plant, formerly used as a styptic. 100 pts. of the fresh plant contain 71·0 water, 10·3 matter soluble in water, 9·2 soluble in dilute potash, 8·9 cellulose, and 1·9 ash free from carbonic acid. The ash contains, in 100 pts., after deduction of carbonic acid, 13·7 potash, 7·7 soda, 27·0 lime, 3·9 magnesia, 0·9 alumina and ferric oxide, 33·9 silica, 4·1 sulphuric anhydride, 7·6 phosphoric anhydride, and 1·2 chlorine.

SANIDIN. Glassy felspar (ii. 620).

SANIDOPHYR. A name given to trachytic porphyry, on account of the crystals of sanidin which are embedded in it.

SANTALIC ACID, SANTALIDE, SANTALIN, &c. (See SANDAL-WOOD, p. 187.)

SANTONIN. *Santonic acid*, $C^{15}H^{18}O^3$.—This substance was discovered in 1830 by Kahler (Brandes. Archiv. xxxiv. 318, xxxv. 216), and about the same time by Alms (*ibid.* xxxiv. 319, xxix. 190), in wormseed, *Semen contra*, *Semen cinæ*, or *Semen Santonici*, the undeveloped flower-heads of *Artemisia Vahliana*, and other species of the same genus. It has been investigated chiefly by H. Trommsdorff (Ann. Ch. Pharm. xi. 90) and W. Heldt (*ibid.* lxiii. 10 and 40). See also Gm. xvi. 250.

To prepare it, a mixture of wormseed, with a small quantity of dry slaked lime is exhausted with hot alcohol, the alcohol expelled by distillation, and the remaining liquid supersaturated with acetic acid. The precipitate thereby formed is purified by solution in alcohol, and treatment with animal charcoal.

Santonin crystallises in flattened hexagonal prisms, or interlaced tufts of crystals, which are colourless at first, but turn yellow on exposure to light. From an ethereal solution it is deposited in rhombic plates: sp. gr. = 1·247. Santonin has very strong lævorotatory power; for the transition-tint $[\alpha] = -230°$ at 20° in alcoholic solution, weaker after addition of alkalis, but not diminished by acids (Buignet, J. Pharm. [3] xl. 252). It is neutral according to Kahler, acid according to Ettling; inodorous; tastes slightly bitter after being kept for some time in the mouth, very bitter in alcoholic solution. It exerts an anthelmintic action, but is sometimes fatal to children when given in quickly-repeated doses of 1 to 2 grains or more (Lavater, Pharm. Viertelj. ii. 110). Larger doses of santonin given to adults produce colour-blindness, lasting for several hours. (Wells, J. Pharm. [3] xv. 111.—Martini, Compt. rend. xlvii. 259; l. 545.)

Santonin gives by analysis 72·40 to 72·6 per cent. carbon, and 7·47 to 7·67 hydrogen, the formula $C^{15}H^{18}O^3$ requiring 73·17 C, 7·32 H, and 29·51 O.

Santonin is nearly insoluble in cold, rather more soluble in hot *water*; very soluble in boiling *alcohol*, less in *ether*. According to Trommsdorff, 1 pt. of santonin requires for solution 43 pts. alcohol at 22·5°, 12 pts. at 50°, and 2·7 pts. at 80°; of ether, 5·75 pts. at 17°, 42 pts. at 40°; of water, 5000 pts. at 17·5°, and 250 at 100°. Santonin dissolves in 4·3 pts. of *chloroform*.(Schlimpert, N. Br. Arch. c. 151); also in *acetic acid* and *volatile oils*.

Santonin melts at 136° to a colourless liquid, which solidifies to a crystalline mass on cooling, but by prolonged fusion, it undergoes a molecular change, and becomes amorphous: the same character is exhibited by many other crystalline resinous bodies—helenin for example. Santonin sublimes without decomposition when heated in small quantities; but when larger quantities are heated, a considerable portion decomposes, yielding an oil, which solidifies on cooling to a brown resinous substance. By prolonged exposure to light, most quickly in alcoholic solution, it is converted into photosantonin, $C^{11}H^{14}O^3$. (Sestini, iv. 627.)

Santonin, suspended in water, and submitted to the action of *chlorine gas*, is converted into mono-, di-, or tri-chlorosantonin, according to the circumstances of the experiment (Sestini). It also yields a crystallisable substitution-product with *bromine*. (Heldt.)

Santonin dissolves without decomposition in strong *sulphuric acid*, and is precipitated from the solution by water; the solution turns red after a while, and yields a resinous substance. According to Kossmann (J. Pharm. [3] xxxviii. 81), santonin boiled with dilute sulphuric acid is resolved into glucose, and a resinous body which he calls santiretin. According to O. Schmidt, however (Zeitschr. f. Chem. [2] i. 212), no such decomposition takes place, even when the ebullition is kept up for a considerable time. If the water be not renewed as it evaporates, the acid, as it becomes concentrated, turns the santonin brown, and converts it into a resinous product—probably dehydrated santonin—which when treated with water and crystallised from alcohol, yields the santonin in its original state. (Schmidt.)

Fuming nitric acid also dissolves santonin; dilute nitric acid converts it, by prolonged ebullition, into a bitter non-crystallisable body, very soluble in water and in alcohol, and finally into a crystallisable acid, also very soluble in water and alcohol, probably succinic acid. Hydrocyanic acid is also formed, together with other volatile products.

Santonin dissolves in *caustic fixed alkalis*, forming definite compounds. It does not appear to combine with ammonia. When it is digested with alcohol and metallic oxides, the liquid assumes a fine crimson colour, which disappears after some time.

The santonates are decomposed by prolonged ebullition, santonin being set free. The *potassium-salt*, obtained like the sodium-salt, forms a gummy mass. The *sodium-salt*, $2C^{15}H^{17}NaO^3.9H^2O$, or $2(C^{15}H^8O^3.NaHO).7H^2O$, is obtained by digesting an alcoholic solution of santonin with sodic carbonate, till the mixture is decolorised; then evaporating to dryness at 30°, exhausting the residue with absolute alcohol to separate the excess of sodic carbonate, and leaving the filtrate to evaporate. It is then deposited in slender interlaced needles, which by crystallisation from a very small quantity of water, are converted into large rhombic prisms, with the dominant faces ∞P, ∞P̆∞, P̄∞. Angle ∞P : P = about 141°; P̆∞ : P̆∞ (brach.) = about 102°. The crystals lose about 7 per. cent. water at 100°. (Heldt.)

The *barium-salt*, $2C^{15}H^8O^3.Ba''H^2O^2.H^2O$ (at 100°), is obtained, by digesting hydrate of barium with alcoholic santonin till the red colour disappears, then filtering, evaporating to dryness at 37·5°, exhausting with water, and again evaporating, as a white crust, slightly gelatinous, and drying up to a light powder.

The *calcium salt*, $2C^{15}H^{18}O^3.Ca''H^2O^2$ (at 100°), obtained in like manner, crystallises in silky needles.

The *lead-salt*, $2C^{15}H^{18}O^3.Pb''O$ (at 120°), is obtained by mixing a boiling alcoholic solution of santonin with neutral acetate of lead, filtering, and exposing the mixture for some time to a temperature of 30° to 40°, avoiding the access of atmospheric carbonic acid. The compound is then deposited in mammellated groups of small nacreous needles.

Santonate of potassium forms a pale-blue precipitate with *cupric salts*, chamois-coloured with *ferric salts*, white with *mercurous*, *silver*, and *zinc salts*; it does not precipitate mercuric salts.

Bromosantonin. When bromine is dropped gradually into a cooled alcoholic solution of santonin, and the liquid is left to evaporate, a brown resin is gradually deposited, together with white, tasteless, inodorous crystals of a brominated santonin, which is very unstable, dissolves with difficulty in water, more easily in boiling alcohol and in ether; also in alcoholic potash, forming a cherry-red liquid. (Heldt.)

Chlorosantonins. (Heldt, Ann. Ch. Pharm. lxiii. 34.—Sestini, Bull. Soc. Chim. 1866, i. 202.)—These compounds are formed by the action of chlorine or of hypochlorous acid on santonin. They are less altered by light in proportion as they contain more chlorine.

Monochlorosantonin, $C^{15}H^{17}ClO^3$, appears to be produced by the action of chlorine-water on excess of santonin. Sestini, by adding half a litre of recently prepared chlorine-water to an equal volume of water holding 10 grms. of santonin in suspension, then shaking the liquid strongly in a closed vessel till the odour of the chlorine was no longer perceptible, and crystallising the product from alcohol, obtained first crystals of santonin, then a confusedly crystalline mass, which turned yellow on exposure to light, but less quickly than santonin, and contained 11·3 per cent. chlorine; -mula of monochlorosantonin requires 12·7 per cent.

Dichlorosantonin, $C^{15}H^{16}Cl^2O^3$.—When santonin suspended in water is exposed to the action of a slow current of chlorine for 10 or 11 hours, a product is obtained which crystallises from alcohol in groups of small laminæ, containing 22·4 per cent. chlorine (Sestini). Heldt, by dissolving santonin in warm hydrochloric acid containing a little alcohol, and adding small crystals of potassic chlorate, stirring all the while, and keeping the liquid warm, obtained a white amorphous mass, which when dissolved in hot alcohol, and crystallised by spontaneous evaporation, yielded delicate white shining needles, which gave by analysis 21·9 per cent. chlorine (it probably contained a small portion of monochlorosantonin).

Dichlorosantonin is insoluble in water, but dissolves easily in *alcohol* and *ether* (Heldt); less easily in alcohol than trichlorosantonin, easily in *chloroform* (Sestini). According to Sestini, it slowly acquires a slight yellow colour, on exposure to light; according to Heldt, it is not altered by exposure to diffused daylight, but when exposed to sunshine, even in an atmosphere of hydrogen, it turns rusty-red, and afterwards becomes covered with a brown crust, but not so quickly as santonin. Alcohol removes the brown crust, leaving white crystals (the effect was perhaps partly due to the monochlorosantonin in Heldt's product). Dichlorosantonin is inodorous and tasteless in the solid state, but very bitter in alcoholic solution. It melts when heated, and solidifies again on cooling; but when heated above its melting-point, it decomposes, with evolution of hydrochloric acid. It dissoles in alcoholic potash, forming an orange-red liquid. (Heldt.)

Trichlorosantonin, $C^{15}H^{15}Cl^3O^3$, was obtained by exposing 60 grms. of santonin suspended in 2½ litres of water to a slow current of chlorine continued for several hours on four successive days, washing the product with tepid water, dissolving it in boiling alcohol, and leaving the solution to evaporate. It crystallises in transparent monoclinic prisms, which are not coloured even by prolonged exposure to sunshine (analysis 34·1 per cent. chlorine; calc. 30·5 per cent.). It is insoluble or nearly so in water, but dissolves with moderate facility in *alcohol*, *ether*, and *chloroform*; from the last-mentioned liquid it crystallises in long silky needles. It does not lose weight by prolonged exposure to air dried by oil of vitriol, or when heated to 100—110°: hence the crystals appear to be anhydrous. It melts at 213°, assuming a faint brown colour. *Alcoholic potash* converts it into colourless or slightly coloured oily drops; and boiling alcoholic solutions of caustic alkalis decompose it, converting it into a resinous substance. (Sestini.)

SANTORIN. An argillaceous mineral, occurring on the island of Santorin, which yields an excellent cement. According to Elsner, it contains 68·5 per cent. silica, 5·5 ferric oxide, 13·3 alumina, 0·7 manganous oxide, 2·3 lime, 3·1 potash, 4·7 soda, with traces of common salt, sodic sulphate, and organic matter.

SAORIA. The seed of *Maesa picta*, a primulaceous plant, used in Abyssinia as a remedy for tapeworm. According to Apoiger (Jahresb. 1857, p. 530), it contains a waxy substance, a soft resin, a fatty non-drying oil, an acrid substance, extractive matter, gum, pectin, albumin, sugar, an iron-greening tannin, lactic acid, citric acid, racemic acid (?), a volatile acid (?), and a volatile oil. The seed dried at 100° yielded 7·7 per cent. ash, containing 27·84 per cent. K^2O, 9·04 Na^2O, 8·76 CaO, 7·47 MgO, 0·98 Al^2O^3, 1·69 FeO, with trace of manganous oxide, 9·00 Cl, 3·73 SO^3, 9·93 P^2O^5, 6·09 SiO^2, 15·17 CO^2, and 0·30 B^2O^3.

SAPAN-RED. *Brazilin.* $C^{22}H^{20}O^7$. (Bolley, Zürich. Mittheil. 1865, p. 2; J. pr. Chem. xciii. 451.)—The colouring matter of sapan-wood (*Cæsalpinia echinata* or *C. Sapan*), appears from Bolley's investigations to be identical with Chevreul's brazilin* (i. 655), obtained from brazil-wood (*Cæsalpinia crista*, *C. brasiliensis*, &c.). It was prepared from a crystalline deposit, which had collected at the bottom of a cask filled with extract of sapan-wood, by dissolving the deposit in absolute alcohol, and leaving the filtrate to crystallise in a vessel excluded from light and air. It is not easily obtained in the pure state from brazil-wood.

Sapan-red, or brazilin, crystallises from absolute alcohol in amber-yellow or brownish rhombohedrons, or in short monoclinic prisms containing 66·66 per cent. carbon and 5·04 hydrogen (calc. 66·66 C, 5·04 H, and 28·28 O); from hydrated alcohol or from aldehyde, in small straw-yellow or golden-yellow monoclinic needles, containing $2C^{22}H^{20}O^7.3H^2O$, turning brown at 90°, and giving off 6·61 per cent. water; no more at 120° ($\frac{3}{2}$ at. H^2O = 6·39 per cent.). They gave by analysis 62·78 per cent. C and 5·48 H (calc. 62·41 C, 5·43 H, and 32·16 O).

Brazilin is soluble in water, alcohol, and ether. The reddish aqueous solution is coloured deep carmine-red by traces of ammonia, the fixed alkalis, or baryta-water. The alcoholic solution, slowly evaporated in contact with air containing ammonia, yields iridescent spangles, which give off ammonia when treated with potash. Brazilin dissolves also in aqueous acid sulphite of sodium, and the solution deposits colourless crystals containing sulphur.

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* The statements respecting brazilin, given (i. 656) on the authority of Preisser, are not to be depended upon.

Brazilin differs from hæmatoxylin (iii. 4) by containing the elements of phenol in addition:

$$\underset{\text{Brazilin.}}{C^{22}H^{20}O^{7}} = \underset{\text{Hæmatoxylin.}}{C^{16}H^{14}O^{6}} + \underset{\text{Phenol.}}{C^{6}H^{6}O}.$$

Accordingly, brazilin treated with nitric acid yields picric acid, whereas hæmatoxylin thus treated yields nothing but oxalic acid.

SAPHIRE. Syn. with SAPPHIRE.

SAPOGENIN. The name given by Bolley (Ann. Ch. Pharm. xc. 211; xci. 117), to the product obtained by boiling saponin with dilute sulphuric or hydrochloric acid. Fremy (Ann. Ch. Phys. [2] lviii. 102), who first obtained this substance, designated it as æsculic acid (i. 59). See also SAPONIN (p. 194), and *Gmelin's Handbook*, xv. 53.

SAPONARIN. A bitter, neutral, crystallisable substance, occurring, according to Osborne (Ann. Phil. xi. 302), in the roots of *Saponaria officinalis*, before flowering time, but not afterwards. It dissolves in less than 2 pts. of water, is soluble also in alcohol and ether, insoluble in oil of turpentine.

SAPONIFICATION. This term was originally applied to the conversion of natural fats (glycerides) into soaps, by the action of alkalis or other metallic hydrates, the change consisting in the rearrangement of the elements of the acting substances in the form of a metallic salt of the fatty acid, and glycerin. It is now, however, used in a wider sense, being extended to the resolution of all ethers, and neutral substances of analogous composition, into acids and alcohols; sometimes even to the decomposition of glucosides under the influence of dilute acids. (See ETHERS, GLUCOSIDES, GLYCERIDES, SOAP.)

SAPONIN. *Struthiin. Githagin. Senegin. Polygalin. Polygalic acid.*—This substance, first observed by Schrade (Gehlen's N. Journ. d. Chem. viii. 548) in the common soapwort (*Saponaria officinalis*), and some time afterwards by Bley (Ann. Ch. Pharm. iv. 283) and Bussy (*ibid.* vii. 168) in the oriental soapwort (*Gypsophila Struthium*), appears to be very widely diffused in the vegetable kingdom. It has been found by O. Henry and Boutron-Charland (J. Pharm. iv. 249) in quillaja-bark (*Quillaja smegmadermos*), by Fremy (Ann. Ch. Pharm. xv. 187) in horse-chestnuts, in which, according to Malapert (J. Pharm. [3] x. 339), it exists chiefly in the ovaries during flowering-time, and in the pericarp of the fruit, immediately after the petals have fallen off. Malapert has also found it in the roots of pinks, in the corn-cockle (*Agrostemma Githago*), the white campion (*Lychnis dioica*), the scarlet lychnis (*L. chalcedonica*); also in *Lychnis Flos cuculi, Silene inflata, Silene nutans, Anagallis arvensis*, and *A. cærulea.*

Saponin is said also to be contained in *Arnica montana, Arum maculatum, Capsella Bursa Pastoris*, the bark of *Gymnoclodeis canadensis*, the root of *Polypodium vulgare*, the fruit of *Sapindus Saponaria, S. laurifolius*, and *S. rigidus*, of *Pircunia abyssinica*, and in many plants of the sapindaceous and mimoseous orders. The irritating extractive matter in the root of the cowslip is, perhaps, identical with saponin.

Senegin, or *Polygalin*, discovered by Gehlen in the root of *Polygala Senega*, which was associated with saponin by Bucholz and Pfaff, minutely examined by Quevenne, who named it *acide polygalique*, is, according to Bolley, probably identical with saponin.

Preparation: A. *From the root of Saponaria*, or of *Gypsophila Struthium.*—1. The chopped root is exhausted with boiling alcohol of specific gravity 0·824; the filtrate is cooled; and the deposit of saponin, which separates after 24 hours, is collected, washed with ether and alcohol, and dried at 100° (Rochleder and Schwarz).—2. The coarsely-pounded root is freed by ether from resin and fat, then boiled with alcohol, and the flocks which separate on cooling and concentration are collected. (Bley and Bussy.)

Saponin prepared from *Gypsophila* is sometimes contaminated with foreign substances. It is purified by dissolving it in the smallest possible quantity of water, and adding baryta-water, which precipitates saponin-baryta, leaving the foreign substances in solution. The white precipitate is washed with baryta-water, and dissolved in water; on passing carbonic acid through the solution, and heating it, carbonate of barium separates out; and after its removal, the saponin may be precipitated by ether-alcohol. (Rochleder and De Payr.)

B. *From Quillaja-bark.*—This, according to Le Beuf, is the best material for preparing saponin for technical purposes. The same process as in A 1 (Le Beuf); or the aqueous extract is boiled with alcohol; the liquid is filtered at the boiling heat; and the white flocks, which fall down on cooling and concentration, are purified by solution in alcohol, with aid of animal charcoal. (Henry and Boutron, Bley.)

C. *From the seeds of the Corn-cockle* (*Agrostemma Githago*).—1. The coarsely pulverised dry seeds are freed from fixed oil by repeated exhaustion with ether, then by once exhausting with cold alcohol of 92° Tralles; the residue is boiled several times with alcohol of 84° Tr.; the liquid is filtered at the boiling heat; and the saponin which separates on cooling is collected, an additional quantity being obtained by mixing the mother-liquor with absolute alcohol. The whole of the saponin thus obtained is dissolved in water; the solution is filtered to separate vegetable gelatin, then precipitated with neutral acetate of lead; the precipitate removed; the filtrate precipitated with basic acetate of lead; the latter precipitate, after thorough washing, decomposed under water by sulphydric acid; and the limpid filtrate evaporated to dryness, or precipitated with absolute alcohol (Scharling).—2. The aqueous extract of the seed is precipitated with sulphate of copper; sulphydric acid is passed through the filtrate; the liquid again filtered, then digested with carbonate of barium; the resulting barium-salts precipitated by alcohol and separated by filtration; and the filtrate either strongly concentrated (in which case the saponin is to be precipitated by absolute alcohol), or evaporated to dryness, and the residue boiled with alcohol of 93° Tr. Saponin thus prepared contains a small quantity of baryta (Scharling).—3. Crawfurd digests the pulverised seeds with warm aqueous alcohol, evaporates the liquid to a syrup, mixes it with wood-charcoal, and dries it completely. The saponin is extracted from the residue by boiling with alcohol.

D. *From Horse-chestnuts.*—The pulverised seeds are exhausted with cold alcohol, and the alcohol is distilled from the tinctures. The yellowish jelly which remains consists, for the most part, of saponin, mixed with fat, a bitter crystallisable substance, and yellow-colouring matter; the fat may be removed by exhaustion with ether. (Frémy.)

E. *From Senega-root:* Senegin, Polygalic acid.—1. The root is exhausted with cold water; the extract concentrated, and filtered from the separated flocks containing senegin and earthy salts; the filtrate precipitated with neutral acetate of lead; the liquid again filtered, freed from lead by sulphydric acid, and evaporated to an extract; this extract exhausted with alcohol of 36°; the tincture evaporated; the residue freed by ether from yellow-colouring matter and fat, then dissolved in water; the solution precipitated with basic acetate of lead; and the precipitate washed and decomposed by sulphydric acid. Part of the senegin then remains with the sulphide of lead, while another portion dissolves, so that:—*a.* The sulphide of lead is collected and boiled with alcohol; *b.* The liquid filtered from the sulphide of lead is evaporated to dryness, and the residue is boiled with alcohol. The hot-filtered tinctures cooled and left to evaporate, deposit senegin, which may be purified, if necessary, by re-solution in alcohol and treatment with animal charcoal (Quevenne). Senega-root exhausted with water still yields senegin when boiled with alcohol, the tincture depositing the senegin when cooled or concentrated. It is purified from fat by ether, then with basic acetate of lead, as above (Quevenne).—2. Bolley precipitates the aqueous solution of officinal extract of senega with neutral acetate of lead; collects and washes the precipitate; decomposes it with sulphydric acid; evaporates the filtrate to dryness; boils the residue with alcohol; evaporates the tincture; treats the residue with ether; dissolves the portion not taken up by the ether in water; precipitates the solution with basic acetate of lead; decomposes the thoroughly-washed precipitate under water with sulphydric acid; evaporates the filtrate; and purifies the senegin which remains by repeated solution in boiling alcohol and cooling.

Properties.—Saponin is a white or nearly white, noncrystalline, friable powder, having a peculiar aromatic odour (Quevenne), inodorous when dry, but having a disagreeable odour when dissolved in water (Scharling). The dust excites violent sneezing. It tastes sweetish at first, then burning and biting, and produces a persistent scratching sensation in the throat. A drop of the aqueous solution introduced into the eye produces violent burning pain, and dilatation of the pupil. Saponin is generally said to be neutral to vegetable colours; but senegin, according to Quevenne, is acid. It acts poisonously on the smaller animals.

The following are analyses of saponin:—

		Rochleder and Schwarz. at 100°.	Overbeck. *mean* at 100°.	Bolley. *mean.*	Crawford.	Rochleder. *mean* at 100°.	Payr. *mean* at 100° *in vacuo.*	Quevenne. *Senegin.*	Bolley. *Senegin.*
Carbon	50·0	52·54	46·81	49·10	50·72	52·64	53·17	54·62	53·58
Hydrogen	7·4	7·26	7·51	6·88	7·44	7·37	7·57	7·53	6·23
Oxygen	42·6	40·20	45·68	44·02	41·84	39·99	39·26	37·85	40·19
	100·0	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

From these discordant results, it is impossible to deduce a formula with certainty; and saponin does not form any definite compounds by the composition of which the analyses might be checked. Rochleder and Schwarz propose for saponin the formula $C^{12}H^{20}O^7$, which requires 52·17 C, 7·24 H, and 40·59 O; Rochleder and v. Payr give for saponin, dried at 100°, $C^{64}H^{106}O^{36}$, requiring 52·97 C, 7·31 H, and 39·72 O. The analyses of senegin agree more nearly with $C^9H^{12}O^5$, requiring 54 C, 6 H, and 40 O; but as neither this substance nor saponin from other sources has been obtained in a perfectly definite state, and as their properties and products of decomposition are essentially the same, it is most probable that senegin is identical with saponin.

Saponin dissolves in *water*, forming a frothy solution, more easily in dilute than in strong *alcohol*, and is insoluble in absolute alcohol, in ether, and in volatile oils: the alcoholic solution does not froth. It is not altered by cold dilute *acids*, and does not unite with them. It dissolves slightly in cold *ammonia* and *potash*, more easily in the same liquids when warm. A solution of saponin in 4 pts. of water forms with *baryta-water* a white precipitate, soluble in excess of saponin or of baryta-water (Bussy); insoluble or nearly so in baryta-water, but easily soluble in pure water (Rochleder and Schwarz). With *neutral acetate of lead*, saponin forms a gelatinous precipitate; and on boiling the filtrate, a further precipitate of pulverulent character is obtained, which swells up during washing. It likewise precipitates *basic acetate of lead*.

Decompositions.—1. Saponin submitted to dry distillation swells up, blackens, and yields a large quantity of acid empyreumatic oil.—2. Boiling *nitric acid* attacks it, forming a yellow resin, mucic acid, and oxalic acid.

Saponin is decomposed by *dilute mineral acids*, slowly in the cold, more quickly when heated, into a carbohydrate and a white precipitate, called sapogenin by Bolley, æsculic acid by Frémy, and regarded by Rochleder and Schwarz as identical with quinovin (p. 32). The composition of this substance has not been precisely ascertained, as its analyses give results varying from 56·9 to 63·2 per cent. carbon, and 8·5 to 8·9 hydrogen; and accordingly various equations have been proposed to explain its formation from saponin. According to Rochleder and Schwarz, the reaction is:—

$$\underset{\text{Saponin.}}{2C^{12}H^{20}O^7} = \underset{\text{Quinovin.}}{C^{12}H^{18}O^3} + \underset{\text{Carbohydrate.}}{C^{12}H^{22}O^{11}}$$

according to Overbeck:—

$$\underset{\text{Saponin.}}{C^{21}H^{38}O^{15}} = \underset{\text{Saporetin.}}{C^9H^{14}O^3} + \underset{\text{Carbohydrate.}}{C^{12}H^{24}O^{12}}$$

according to Bolley:—

$$\underset{\text{Saponin.}}{2C^{18}H^{24}O^{10}} + 5H^2O = \underset{\text{Sapogenin.}}{C^{12}H^{18}O^5} + \underset{\text{Carbohydrate.}}{4C^6H^{10}O^5}.$$

According to Rochleder and v. Payr (Wien. Akad. Ber. xlv. 7), saponin, when decomposed by acids, is capable of yielding various products of decomposition, according as, of the 6 at. carbohydrate which it may be supposed to contain, two, more than two, or the whole are separated. The products resulting from partial separation are obtained by the action of aqueous acids, but complete decomposition is produced only by the action of alcoholic hydrochloric acid (Rochleder and v. Payr). According to this, only the crystals described under *d* are the true sapogenin.

a. The product obtained from saponin, $C^{64}H^{106}O^{36}$, by elimination of 2 at. carbohydrate ($C^6H^{12}O^6$), is perhaps Frémy's æsculic acid (i. 59), as it agrees in amount of carbon with the formula $C^{52}H^{82}O^{24}$ (calc. 57·25 per cent. C and 7·52 H). (Rochleder.)

b. Saponin purified with baryta-water yields, when heated with aqueous hydrochloric acid, 53·1 per cent. sugar, and gelatinous flocks, which, when dried at 100°, contain, on the average, 65 per cent. C and 8·64 H, agreeing nearly with the formula $C^{40}H^{62}O^{14}$ (calc. 62·66 per cent. C and 8·09 H). In this case the decomposition takes place chiefly in the manner shown by the equation:

$$C^{64}H^{106}O^{36} + 2H^2O = C^{40}H^{62}O^{14} + 4C^6H^{12}O^6$$

(calc. 49·62 per cent. $C^{12}H^{12}O^{12}$).

c. By prolonged boiling with aqueous hydrochloric acid, 62·66 per cent. sugar and a $C^{34}H^{52}O^9$, are obtained (calc. 67·55 per cent. C and 8·61 H):

$$C^{64}H^{106}O^{36} + 3H^2O = C^{34}H^{52}O^9 + 5C^6H^{12}O^6,$$

(calc. 59·8 per cent. $C^{12}H^{12}O^{12}$).

d. When the flocks which separate on boiling saponin with aqueous hydrochloric acid, are dissolved in anhydrous alcohol, and hydrochloric acid gas is passed for several hours through the boiling solution, white crystals, $C^{28}H^{42}O^4$, are deposited, produced by complete resolution of the saponin (Rochleder and v. Payr):

$$C^{64}H^{106}O^{36} + 4H^2O = C^{28}H^{42}O^4 + 6C^6H^{12}O^6.$$

These crystals, after recrystallisation from alcohol and drying at 100°, contain, on the average, 75·78 per cent. C, 9·76 H, and 14·46 O (calc. for $C^{28}H^{42}O^4$, 76·02 per cent. C, 9·50 H, and 14·48 O). They are insoluble in water, dissolve sparingly in cold, easily in hot alcohol, and are nearly insoluble in aqueous potash. From the easily-produced solution in alcoholic potash, aqueous potash throws down almost the whole of the compound of sapogenin and potash, which gives up its potash during washing. (Rochleder and v. Payr.)

The carbohydrate produced together with sapogenin, is insoluble in alcohol at the moment of separation, and is converted into dextroglucose only by the prolonged action of hot acids. (Rochleder and v. Payr.)

When saponin from horse-chestnuts is treated with *potash-ley*, a compound of potash with a yellow-colouring matter contained in the saponin is first formed; afterwards sapogenin-potash (æsculate of potassium), from the solution of which the sapogenin is thrown down by acids (Frémy). Saponin from soapwort treated in like manner does not yield sapogenin (Frémy). Aqueous saponin boiled with potash-ley, then mixed with hydrochloric acid, yields a white, tolerably abundant, non-gelatinous precipitate of sapogenin (Quevenne). Saponin mixed with potash-ley and evaporated turns brown, and the residue forms, with water, a brown solution, from which acids do not precipitate Frémy's æsculic acid (Rochleder and Schwarz). By the action of potash upon saponin, a finely-crystallised acid and an amorphous substance are obtained, the latter being resolved by hydrochloric acid into two products. (Rochleder and v. Payr, Wien. Akad. Ber. xxiv. 42.)

Saponin boiled with an alkaline solution of *cupric oxide*, throws down a small quantity of cuprous oxide (Bolley). According to Scharling, it forms, with cupric sulphate and potash, a blue-green precipitate, without reducing the cupric oxide.

SAPONITE. Syn. with SOAPSTONE.

SAPORETIN. $C^9H^{14}O^2$? The substance produced, according to Overbeck, together with sugar, by boiling saponin with dilute acids (p. 194).

SAPPARE, SAPPARITE. Syn. with KYANITE (iii. 449).

SAPPHIRE. See CORUNDUM (ii. 86). Deville and Caron have produced sapphires artificially, by exposing a fluoride of aluminium mixed with a little fluoride of chromium to a white heat, in a crucible made of alumina and enclosing a small platinum dish containing boric anhydride. (Compt. rend. xlvi. 764; Jahresb, 1858, p. 2.)

SAPPHIRE-QUARTZ. Quartz from Gölling, in the Salzburg territory in Upper Austria, coloured blue by admixed crocidolite.

SAPPHIRIN. A hard blue mineral occurring, with mica and anthophyllite, at Fiskenaes, in Greenland Its structure is granular massive; hardness = 7·8; specific gravity = 3·42—3·48; lustre vitreous. It is translucent, and exhibits colours by polarised light: probably trimetric.—*Analyses: a.* by Stromeyer (Gilb. Ann. lxiii. 374); *b.* by Damour (Bull. Geolog. de Fr. [2], vi. 315):—

SiO^2.	Al^2O^3.	MgO.	FeO.	MnO.	CaO.	Loss by ignition.		
14·51	63·10	16·85	3·92	0·53	0·38	0·49	=	99·78
14·86	63·25	19·28	1·99				=	99·38

These results agree approximately with the formula $(2Al^2O^3.3SiO^2).6(MgO.Al^2O^3)$.

SAPROCHROME. *Saprocyanogen. Saprocyanin* (from σαπρός putrid, χρῶμα colour, κύανος blue). A blue or red colouring matter, produced by the putrefaction of certain *Oscillatoriæ*. (Nees v. Esenbeck, Ann. Ch. Pharm. xvii. 76; Handw. vii. 244.)

SAPUCAIA. *Lecythis urnigera.*—A Brazilian tree of the myrtaceous order, producing a bottle-shaped fruit. The juice (*sapucaia-wine*), which flows from incisions in old trees, contains in 1000 pts.: 91·2 pts. free acetic acid, 27·4 uncrystallisable sugar, 3·9 iron-blueing tannin, 40·0 gum and extractive matter, with traces of gallic acid, 9·9 potassic and calcic acetates. The shell of the fruit contains a tannin (lecythitannic acid), which appears to be related to quercitannic acid, and in the older fruits is converted into a brown substance (*sapucaia-brown*), soluble in hot water and in alcohol.

The fatty oil of sapucaia-nuts, amounting to about 39 per cent., is non-drying, and resembles oil of almonds. (Peckolt, J. Pharm. [4] i. 319.)

SARACENIA. The root and leaves of *Saracenia purpurea* (a plant of frequent occurrence in Canada and the northern states of the American Union, and recommended as a remedy against smallpox) contain, besides the usual plant-constituents, a volatile acid (acrylic acid) and 0·18 per cent. of a base (not yet examined) which smells like conine, and is volatile at ordinary temperatures. (Björklund and Dragendorff, Russ. Zeitschr. Pharm. ii. 317, 344, 369.)

SARCINE. $C^5H^4N^4O$. (Strecker, Ann. Ch. Pharm. cii. 294; cviii. 129.)—A weak organic base, existing in the juice of muscular flesh. It is isomeric with Scherer's hypoxanthine, and Scherer is of opinion that the two are identical. According to Strecker, however, sarcine is distinguished from hypoxanthine by its crystalline character, its greater solubility in water and in cold hydrochloric acid, and by not being decomposed when dissolved in nitric acid. Probably hypoxanthine is impure sarcine, or a mixture of that substance with xanthine (*q. v.*).

Sarcine is found in the mother-liquor of the preparation of creatine. It has hitherto been obtained only from the flesh of oxen and horses; 100,000 pts. of beef yield 22 pts. of sarcine. Human urine sometimes contains a body which is perhaps sarcine, and perhaps also guanine, $C^5H^5N^5O$ (= sarcine + NH).

Preparation.—Sarcine is separated from the hot dilute mother-liquors obtained in the preparation of creatine, by precipitation with cupric acetate (or better with silver-nitrate). The precipitate, which contains a compound of sarcine with the metallic oxide or salt, together with foreign substances, is washed on a filter with boiling water and decomposed by sulphydric acid; the filtrate is evaporated; and the coloured sarcine which separates is purified by solution in hot water, with addition of hydrate of lead, precipitation of the filtrate with sulphydric acid, and evaporation.

Properties.—Sarcine separates from aqueous solution as a white indistinctly crystalline powder, which does not melt at 150°, but decomposes at higher temperatures, giving off hydrocyanic acid and a white sublimate (cyanuric acid?) It dissolves in 300 pts. of cold and 78 pts. of boiling water, and in 900 pts. of boiling alcohol. The solutions do not redden litmus. In hydrochloric acid, potash, ammonia, and baryta-water, it dissolves more easily than in water. Strong sulphuric acid and nitric acid also dissolve it easily, without colouring or evolution of gas; but when evaporated with excess of nitric acid, and somewhat strongly heated, it yields a yellow residue, which is turned red by potash: this reaction is likewise exhibited by hypoxanthine, guanine, and xanthine.

Sarcine forms definite compounds, both with acids and with metallic bases. A solution of sarcine in boiling hydrochloric acid yields colourless, nacreous, tabular crystals of the *hydrochlorate*, $C^5H^4N^4O.HCl.H^2O$.—The *chloroplatinate*, $2(C^5H^4N^4O.HCl)PtCl^4$, is a yellow crystalline precipitate.—The *nitrate* forms transparent crystals, resembling acetate of sodium, which become opaque on exposure to the air, and are turned milk-white and decomposed by water. The *sulphate* is precipitated by alcohol from a solution of sarcine in strong sulphuric acid, in needle-shaped crystals, likewise decomposible by water.—*Urate of Sarcine*, $C^5H^4N^4O.C^5H^4N^4O^3$, is precipitated by urate of potassium from the solution of the hydrochlorate. It is distinguished from xanthine, $C^5H^4N^4O^2$, with which it is polymeric, by the behaviour of its nitric acid solution with nitrate of silver, forming therewith a copious white precipitate, which dissolves but slowly at the boiling heat, whereas the solution of xanthine in nitric acid is not precipitated by nitrate of silver.

A solution of sarcine in boiling *baryta-water* mixed with a cold-saturated solution of baryta, deposits the compound, $C^5H^4N^4O.Ba''H^2O^2$, in colourless crystals. From solution in caustic *potash*, sarcine is for the most part precipitated by carbonic acid. The compounds of sarcine with *zinc-oxide*, *cupric oxide*, and *mercuric oxide*, are flocculent precipitates, insoluble in water. With *nitrate of silver*, sarcine forms a white flocculent precipitate, insoluble in cold nitric acid, and crystallising from hot nitric acid in scales having the composition $C^5H^4N^4O.AgNO^3$. An ammoniacal solution of nitrate or chloride of silver forms with solution of sarcine, a gelatinous precipitate consisting of $C^5H^4N^4O.Ag^2O$, which contracts strongly in drying, and is insoluble in ammonia. These silver-precipitates may be used for the purification and quantitative estimation of sarcine.

SARCOCOLLA. A gum-resin collected in Ethiopia and at the Cape of Good Hope, probably from *Penacca mucronata*, *P. Sarcocolla*, and *P. squamosa*. It forms yellow irregular grains of various size, and more or less aggregated; is inodorous; has a sharp and sweetish-bitter taste; swells up strongly when heated, without completely melting; and burns with an odour like that of caramel. It consists chiefly of resin, gum, and **sarcocollin**, a body resembling glycyrrhizin, which may be separated by extracting the resin with ether and treating the residue with alcohol, which dissolves the sarcocollin and leaves the gum.

Sarcocollin remains, on evaporating the alcoholic solution, as a brownish, semitransparent, amorphous mass, which has a sweetish and afterwards bitter taste, softens without melting when heated, and finally burns away, almost without residue, emitting an odour of burnt sugar. It dissolves in 40 pts. of cold and 25 pts. of boiling water. Its solution, saturated when hot, deposits a syrupy liquid no longer soluble in water (a property which seems to indicate that sarcocollin is a mixture). Alcohol dissolves it in almost all proportions, forming a solution which is clouded but not precipitated by water. Sarcocollin contains, according to Pelletier (Ann. Ch. Pharm. vi. 32), 57·13 per cent. carbon, 8·34 hydrogen, and 34·31 oxygen. According to Johnston, it is a mixture of several resins, which may be separated by bases. Acetate of lead throws down from the alcoholic solution, a lead-salt containing the compound $C^{20}H^{30}O^{8}$; and the filtrate yields with ammonia a further precipitate, which has not been analysed.

SARCOCOLLIN. See the last article.

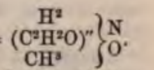
SARCOLITE. A mineral from Vesuvius, occurring in small flesh-coloured or reddish-white quadratic crystals, exhibiting the combination $P . \frac{1}{3}P . 3P . \infty P . P\infty . \infty P\infty . \infty P . 3P3 . P3$, the last occurring hemihedrally, as a pyramid of the third order. Angle $oP : P = 128° 45'$; $oP : P\infty = 138° 27'$ (Rammelsberg, Pogg. Ann. cix. 570). The crystals are translucent, and have a vitreous lustre. Hardness = 5·5 to 6·0. Specific gravity = 2·545 (Scacchi); 2·932 (Rammelsberg). Melts before the blowpipe to a white enamel, and is decomposed by acids, with separation of gelatinous silica.

Analyses: *a.* by Scacchi (Mem. min. e geol., Napoli, 1841—1843).—*b.* by Rammelsberg (*loc. cit.*):

	SiO^2	Al^2O^3	CaO	Na^2O	K^2O		
a.	42·11	24·50	32·43	2·93		=	101·97
b.	40·51	21·54	32·36	3·30	1·20	=	98·91

Rammelsberg's analysis may be represented by the formula $3[2(Ca''O ; Na^2O ; K^2O).SiO^2]$, $(2Al^2O^3.SiO^2)$ or $3(Ca'' ; Na^2 ; K^2)^2SiO^4.\overset{\prime\prime\prime}{Al^4}Si^3O^{12}$, included under the general formula of garnet, $3M^4SiO^4.\overset{\prime\prime\prime}{Al^4}Si^3O^{12}$. For 6 at. SiO^2, 2 at. Al^2O^3, 5·4 at. $Ca''O$, and 0·6 at. Na^2O, the formula requires 40·41 per cent. silica, 22·45 alumina, 33·05 lime, and 4·09 soda.

The name **sarcolite** was also applied by Vauquelin to gmelinite.

SARCOSINE. $C^3H^7NO^2$ = *Methyl-glycocine*, $C^2H^4(CH^3)NO^2$ = 

$$\left.\begin{matrix} H^2 \\ (C^2H^2O)'' \\ CH^3 \end{matrix}\right\} \begin{matrix} N \\ O \end{matrix}.$$

(Liebig, Ann. Ch. Pharm. lxii. 310.—Dessaignes, Compt. rend. xli. 1258.—Volhard, Ann. Ch. Pharm. cxxiii. 261.)—A weak organic base, metameric with alanine, lactamic acid, and urethane or ethylic carbamate. It is produced: 1. Together with urea (carbamide), by the action of baryta on creatine:

$$\underset{\text{Creatine.}}{C^4H^{11}N^3O^3} = \underset{\text{Sarcosine.}}{C^3H^7NO^2} + \underset{\text{Urea.}}{CH^4N^2O}.$$

The urea may be detected in the liquid during the progress of the reaction, but is almost immediately resolved into carbonic acid and ammonia (Liebig).—2. By the action of methylamine on monochloracetic acid, just as glycocine is formed by treating that acid with ammonia (Volhard):

$$C^2H^3ClO^2 + CH^5N = HCl + C^3H^7NO^2.$$

Preparation.—1. Ten parts of baryta-crystals (free from potash, soda, lime, chlorine, and nitric acid, which substances are difficult to separate from sarcosine) are added to a boiling saturated solution of 1 pt. of creatine in water, the mixture being kept boiling and the water and baryta renewed, as long as ammonia continues to escape, and a precipitate of barytic carbonate to form; the liquid is filtered from this precipitate; the caustic baryta precipitated by a stream of carbonic acid gas, and the filtrate evaporated to a syrup: this syrup, when set aside, solidifies to a heap of transparent and colourless crystalline laminæ. To purify the product, the mass is dissolved in excess of dilute sulphuric acid; the solution evaporated to a syrup over the water-bath; the syrup mixed with alcohol by stirring the two together with a glass rod, till the mixture is converted into a white cyrstalline powder of sulphate of sarcosine; the powder is washed with cold alcohol (which dissolves out a substance resembling urethane), dissolved in water, and heated with carbonate of barium till the liquid becomes neutral, and the filtrate is evaporated over the water-bath to a syrup, which crystallises in 24 to 36 hours.

2. Ethylic chloracetate is heated in a sealed tube to 120°—130°, with excess of concentrated aqueous methylamine, whereby the chloracetic acid is completely decomposed, and hydrochlorate of methylamine is produced, together with sarcosine. The liquid is then boiled with baryta-water till the whole of the methylamine is distilled off, and the remaining solution is freed from baryta by sulphuric acid, and evaporated to a syrup. Hydrochlorate of sarcosine then separates in a crystalline mass, which must be pressed between paper and dissolved in boiling alcohol, whence it separates in shining needles. On decomposing this salt with carbonate of silver, treating the filtrate with animal charcoal, and evaporating, sarcosine separates in crystals after a few days.

Properties.—Sarcosine forms trimetric crystals, $\infty P . \bar{P}\infty$, with the faces P and oP, less frequent and but slightly developed. Angle $\infty P : \infty P = 77°$ (Kopp). They are rather large, colourless, and perfectly transparent, very soluble in water, slightly soluble in alcohol, insoluble in ether. They preserve their appearance unaltered at 100°, but melt at a higher temperature and volatilise without residue.

Sarcosine heated with soda-lime gives off methylamine. The aqueous solution of the sulphate is decomposed by peroxide of lead, with brisk effervescence, yielding an alkaline solution, which contains methylamine. (Dessaignes.)

The aqueous solution of sarcosine is neutral to vegetable colours, and has an acrid, sweetish, slightly metallic taste. It does not precipitate a solution of silver-nitrate or mercuric chloride; but a crystal of sarcosine introduced into a cold saturated solution of *mercuric chloride* dissolves readily, and soon forms numerous delicate needles of a double salt, which ultimately converts the liquid into a solid mass. A solution of *cupric acetate* is coloured dark-blue by sarcosine in the same manner as by ammonia, and the liquid yields by evaporation thin laminæ of a double salt having the same colour.

Hydrochlorate of Sarcosine.—Sarcosine evaporated with hydrochloric acid yields a white mass, which crystallises from alcohol in small transparent needles. The solution mixed with excess of platinic chloride, yields, by spontaneous evaporation, large, honey-yellow, octahedral segments of a *platinum-salt*, which, when freed from excess of platinic chloride by washing with ether and alcohol, contains $2(C^3H^7NO^2.HCl).PtCl^4.2H^2O$: it gives off its water at 100°.

The *sulphate*, $2C^3H^7NO^2.H^2SO^4$, prepared as above (p. 198), dissolves in 10 to 12 pts. of boiling alcohol, and separates on cooling in transparent, colourless, highly lustrous, four-sided plates, resembling chlorate of potassium. It gives off its water (6·8 per cent.) at 100°, dissolves readily in water, forming an acid solution, very slightly in cold alcohol. From the aqueous solution it crystallises in large plumose laminæ. (Liebig.)

SARD. A deep brownish variety of chalcedony, of a blood-red colour by transmitted light.

SARDACHATES. The ancient name of a variety of agate, containing layers of sand or cornelian.

SARDONYX. Onyx consisting of layers of sand and white chalcedony.

SARSAPARILLA-ROOT. The root of the South American *Smilax Sarsaparilla*, *Sm. syphilitica*, or *Sm. officinalis*, and probably of other species of the same genus. It contains, besides gum, starch, &c., a peculiar substance, variously designated as parallin, pariglin, parallic acid, salsaparin, sarsaparillin, and smilacin.

SARSAPARILLIN. This substance, first extracted from sarsaparilla by Pallota (Schw. J. xliv. 147), and further studied by Poggiale (Ann. Ch. Pharm. xiii. 84), Thubeuf (*ibid.* xiv. 76), and Petersen (*ibid.* xv. 74; xvii. 166), is deposited in the crystalline form from the concentrated alcoholic extract of the root, previously decolorised by animal charcoal. and may be purified by recrystallisation. It forms colourless inodorous needles, very soluble in water and alcohol at the boiling heat, less soluble at ordinary temperatures, soluble also in ether and volatile oils, slightly soluble in fixed oils. The solutions froth when agitated. The crystals contain 8·56 per cent. water, which they give off at 100°. The dried substance gives by analysis from 62·1 to 63·6 per cent. carbon, and 8·4 to 9·8 hydrogen. Sarsaparillin is decomposed by nitric acid. Strong sulphuric acid dissolves it with deep red colour, changing to violet, and ultimately to yellow. Water precipitates it unaltered. (See PARIGLIN, *Handw. d. Chem.* vi. 94.)

SASSAFRAS-OIL. A volatile oil obtained from the bark and wood of the root of *Laurus Sassafras.* It has a faint yellow colour, a peculiar odour like that of fennel, and an acrid taste. Specific gravity = 1·09. When distilled, it begins to give off vapour at 115°, but the boiling-point quickly rises to 228°, where it remains stationary, and a slightly brown-yellow residue remains in the retort.

Oil of sassafras is a mixture of two bodies. When exposed to a freezing mixture (composed of 12 pts. ice, 5 pts. common salt, and 5 pts. nitrate of ammonium), it becomes filled with bulky crystals of a camphor or stearoptene, containing 73·9 per cent. carbon and 6·4 hydrogen, agreeing nearly with the formula $C^{10}H^{10}O^2$. Vapour-density of the crystals: obs. = 5·800—5·956: calc. = 5·67.

Bromine acts strongly on oil of sassafras, hydrobromic acid being copiously evolved, and a crystalline mass formed, consisting of $C^{10}H^8Br^2O^2$. The action of *chlorine* is less definite. According to Faltin (Ann. Ch. Pharm. lxxxvii. 376), it eliminates a large quantity of hydrochloric acid, and forms a viscous mass, which, when neutralised with milk of lime, yields a small quantity of common camphor (perhaps formed from the liquid which, together with the crystalline compound above mentioned, constitutes oil of sassafras).

Pentachloride of phosphorus attacks oil of sassafras strongly, and the product distilled in an oil-bath yields at 238° an oily liquid, holding in solution phosphoric oxychloride, from which it may be freed by washing. When purified by rectification over massicot in a current of carbonic anhydride, it contains $C^{10}HCl^9O^2$. (St. Evre, Ann. Ch. Phys. [3] xii. 107.)

Oil of sassafras is inflamed by *fuming nitric acid;* with acid of ordinary strength it forms a yellow resin; with dilute nitric acid it yields oxalic acid.

Sulphuric anhydride, or *strong sulphuric acid*, attacks the oil violently, often setting it on fire. The product is a red resin, often accompanied by deposited carbon (see SASSARUBRIN); on diluting with water, and saturating with carbonate of barium, a resinous salt is obtained. The oil subjected to the prolonged action of a current of *sulphurous anhydride*, turns yellow, and becomes hot, the colour afterwards changing to green, and finally to orange-yellow. Sulphur is then deposited, and the liquid, when left at rest, separates into two layers, the upper consisting of undecomposed sassafras-oil, and the lower of a new oil distilling at 235°, and consisting, according to St. Evre, of $C^{10}H^{10}O^3$.

When oil of sassafras is passed through a red-hot tube, or over potash-lime, naphthalene is produced, together with phenol. According to St. Evre, it may be distilled without alteration over phosphoric anhydride, chloride of zinc, potassium, or a mixture of sulphuric acid and dichromate of potassium.

SASSAFRAS-ROOT. The root-bark of *Laurus Sassafras*, a North-American tree, contains, according to Reinsch (Repert. Pharm. xxxix. 180), in 100 pts., 6·6 pts. of substances extractable by ether (light and heavy essential oil, camphoroïdal and tallow-like substance, balsamic resin and wax), 15·0 pts. by strong alcohol (consisting of 9·2 sassafrid and 5·8 tannic acid), 6·8 pts. by weaker alcohol (gum, sassafrid, and tannic acid), 3·6 by cold water, 5·4 by boiling water, 28·9 by potash-ley, and 33·7 pts. vegetable fibre. The wood of the root contains similar constituents, but in much smaller quantity.

SASSAFRID. A constituent of the root-bark of *Laurus Sassafras*, which may be extracted by alcohol, after the bark has been freed by ether from volatile oil, wax, &c. The sassafrid is separated from the alcoholic solution by water, and when recrystallised from alcohol, forms yellow-brown crystalline grains, which easily make marks like chalk, and have neither taste nor smell. When heated in the air it swells up, emitting a pungent odour; by distillation it gives off white vapours, condensing to a white powder, which forms a blue-green precipitate with ferric salts. Cold water has but little action on sassafrid; hot water forms a red-brown solution, which becomes turbid on cooling. In ether sassafrid dissolves slowly, with wine-yellow colour; nitric acid converts it into oxalic acid and an oily body. The concentrated solution of sassafrid is precipitated by lime-water, baryta-water, and various metallic salts; dilute sulphuric and nitric acids render its colour lighter; tincture of galls and ferrocyanide of potassium have no effect upon it.

SASSAFRIN. See SASSARUBRIN.

SASSA-GUM. *Pseudo-tragacanth.* A gum obtained from *Inga Sassa*, an Abyssinian plant. It swells up in water, like gum-tragacanth, but does not form so thick a mucilage. It is also mixed with a much greater proportion of starch-granules, so that it is coloured dark-blue by iodine.

SASSAPARILLA. Syn. with SARSAPARILLA.

SASSARUBRIN. A resin produced, according to Hare (Sill. Am. J. xxxiii.

285), by the action of sulphuric acid on sassafras-oil. When equal volumes of alcohol, sulphuric acid, and sassafras-oil are heated together, a red tumefied mass is formed, consisting of a compound of sassarubrin and sulphuric acid; and on treating this resin with ammonia, and washing, sassarubrin remains as a tasteless mass, which is soluble in alcohol and in ether, and colours sulphuric acid red, even in small quantity. Precisely similar actions are exhibited by the oils of cloves and cinnamon.

When the oily mixture of sulphuric acid, alcohol, and sassafras-oil is heated, there is evolved at first a yellowish liquid, designated by Hare as sassafrin, which, when freed from sulphurous acid by ammonia, and from admixed ether by heat, is neutral, and has an odour different from that of sassafras-oil.

SASSOLIN, or **SASSOLITE.** Native boric acid, BH^3O^3, occurring more or less pure in irregular six-sided laminæ belonging to the triclinic system, or as a crust, or in stalactitic forms composed of small scales. It is white, or yellowish (when tinged by sulphur), has a nacreous lustre, a specific gravity of 1·48, and is easily friable. It occurs, as a deposit from hot springs or ponds, in the lagunes of Tuscany, abundantly also in the cràter of Vulcano, one of the Lipari Isles, forming a layer on the sulphur; it was first found near Sasso, whence its name.

SATERSBERGITE. This name has been given to native arsenide of iron, $FeAs^2$, from Fossum in Norway.

SATURATION. A liquid is said to be saturated with a solid or a gas when it has taken up the maximum quantity of that solid or gas which it is capable of dissolving under the existing circumstances. The quantity of a salt, or other solid, which a given liquid is capable of dissolving, depends upon its temperature, and, for the most part, increases with the temperature, so that a solution saturated at a given temperature is no longer saturated at a higher temperature, and, on the other hand, deposits a portion of the dissolved solid when the temperature falls.

The quantity of a gas which a liquid can dissolve depends upon both temperature and pressure, increasing for the most part directly with the pressure, and diminishing as the temperature rises, so that a solution saturated at a given pressure and temperature gives off a portion of the gas when the pressure is diminished, or the temperature rises. (See Gases, Absorption of, ii. 790.)

With reference to the composition of salts, the word saturation is equivalent to neutralisation, an acid being said to be saturated with a base, when it unites with the quantity of that base required to form a neutral or normal salt.

SATURATION, CAPACITY OF. A term employed by Berzelius to denote the quantity of oxygen which must be contained in a base in order to form a neutral salt with 100 pts. by weight of an anhydrous oxygen-acid or anhydride. Thus, as in the neutral sulphates, the oxygen of the anhydrous acid is to that of the base as 3 : 1, in the neutral nitrates as 5 : 1, in the neutral carbonates as 2 : 1, in the acetates as 3 : 1, &c.; and as, moreover, 100 pts. of sulphuric anhydride contain 60 pts. oxygen, 100 pts. nitric anhydride 74·07 oxygen, 100 pts. carbonic anhydride 72·72 oxygen, 100 pts. acetic anhydride 47·06 oxygen, &c., it follows that the saturating capacity of sulphuric acid is $\frac{60}{3} = 20$; of nitric acid $\frac{74{\cdot}07}{5} = 14{\cdot}81$; of carbonic acid $\frac{72{\cdot}72}{2} = 36{\cdot}36$; of acetic acid $\frac{47{\cdot}06}{3} = 15{\cdot}69$.

SATURNUS. By this name the alchemists originally distinguished lead and its compounds, *Acetum Saturni, Saccharum Saturni, Cinis Saturni*, &c., probably because lead easily fuses with other metals, and devours them, as it were, as Saturn is said to have devoured his children.

SAUALPITE. Syn. with Zoisite.

SAULDAMMAR, or *Dhara Dammar*, is the name of a resin collected in the northern parts of Hindostan from the saul-tree, *Shorea robusta*.

SAUSSURITE. *Lemantite. Felsite. Jade tenace. Feldspath tenace. Albite compacte. Bitterstein.*—A mineral allied to labradorite, occurring in crystallo-granular or compact masses, sometimes with labradorite, sometimes in place of it, as a constituent of euphotide, hypersthenite, diabase, gabbro, and other similar rocks. It exhibits indistinct cleavage in two directions, parallel to the faces of a rhombic prism of 24° nearly. Hardness = 5·5 to 6·0. Specific gravity = 3·2 to 3·4. Colour grey, greenish, reddish, or bluish. Dull, or with a faint lustre. Subtranslucent. Fracture splintery to uneven. Extremely tough. Before the blowpipe it melts with great difficulty to a greenish-grey glass. It is not acted upon by acids.

Analyses.—*a.* From the Lake of Geneva (M. de Saussure, Journ. des Mines, xix. 205).—*b.* From the same (Klaproth, *Beiträge*, iv. 271).—*c.* From Mont Genevre: greenish-white; specific gravity = 2·65 (Boulanger, Ann. Min. [3] viii. 159).—*d.* From the Orezza valley, Corsica: easily fusible before the blowpipe (Boulanger). *e.* From Switzerland: bluish-white; specific gravity = 3·365 (Hunt, Sill. Am. J. [2] xxvii. 336).—*f.* From the euphotide of the Lake of Geneva: finely granulo-crystalline; greyish to bluish-white; specific gravity = 3·227 (Fikenscher, Jahresb, 1863, p. 811):

	SiO^2	Al^2O^3	Fe^2O^3	Mn^2O^3	CaO	MgO	Na^2O	K^2O	Loss by ignition		
a.	44·00	30·00	12·50	0·05	4·00	. .	6·00	0·25	. .	=	96·80
b.	49·00	24·00	6·50	. .	10·50	3·75	5·50	. .	. .	=	99·25
c.	44·6	30·4	. .	. .	15·5	2·5	7·5	. .	. .	=	100·5
d.	43·6	32·0	. .	. .	21·0	2·4	. .	1·6	. .	=	100·6
e.	43·59	27·72	2·61	. .	19·71	2·98	3·08	. .	0·35	=	100·04
f.	45·34	30·28	1·37	. .	13·87	3·38	4·73	. .	0·71	=	99·68

These analyses may be represented by the general formula $3(M^4;\overset{\prime\prime}{M}{}^2)SiO^4.2\overset{\prime\prime\prime}{M}{}^4Si^3O^{12}$, similar to that of mejonite, which however contains no alkali.

The name *Saussurite* has been extended to other constituents of the above-mentioned rocks, of similar character, but containing a larger proportion of silica (48 to 54 per cent.) (See *Rammelsberg's Mineralchemie*, p. 605; and Jahresb. 1861, p. 997.)

SAVINE, OIL OF. *Sädebaumol, Sevenbaumöl.*—A volatile oil obtained by distilling with water the berries and the herb of the savine (*Juniperus Sabina*). According to Dumas, it is polymeric with oil of turpentine, $C^{10}H^{16}$. It is a nearly colourless mobile oil, which partly resinises on exposure to the air, becoming yellow and somewhat viscid. It has a pungent disagreeable odour, and a sharp, aromatic, camphor-like taste. Specific gravity = 0·91 to 0·94. Absolute alcohol dissolves it in all proportions; with 2 pts. of highly rectified spirit it forms a clear solution; with 3 pts. or more, an opalescent solution. It detonates with iodine, and is converted by nitric acid into a reddish-yellow balsam. When mixed with an equal quantity of strong sulphuric acid, it yields, according to Winckler (Repert. Pharm. [2] xlii. 330), a fourth of its weight of an oil, which after distillation over potash, is very much like oil of thyme. According to Zeller (N. Jahresb. f. Pharm. xii. 1), the fresh herb of savine yields 1½ per cent. of the oil; the dry herb 2 per cent.; the fresh berries 10 per cent.

SAVITE. A mineral occurring in the gabbro of Tuscany, forming thin dimetric prisms [trimetric, according to Breithaupt, Berg- u. hüttenm. Zeit. 1855, p. 223] of 91° 41′, colourless, transparent, having a hardness = 3·3, and specific gravity = 2·450. Melts with great difficulty before the blowpipe. According to Bechi (Sill. Am. J. [2] xiv. 64), it contains 49·17 per cent. silica, 19·66 alumina, 13·50 magnesia, 10·52 soda, 1·23 potash, and 6·57 water (= 100·65), agreeing approximately with the formula $(\overset{\prime\prime}{M}g^2Na^2)Si^3O^9.\overset{\prime\prime\prime}{A}l^2SiO^5.2H^2O$. According to a new examination of the crystals by Quintino Sella (*N. Cimento*, March 1858), the formula agrees exactly with that of natrolite.

SAYNITE. Syn. with Bismuth-nickel (i. 596).

SCABIOSA. A genus of dipsaceous plants, three species of which have been chemically examined by Sprengel (J. f. techn. Chem. viii. 311, 373; ix. 1), with the following results:—

In 100 parts:	*Scabiosa succisa.*	*Scabiosa arvensis.*	*Scabiosa columbaria.*
Water	83·0	80·0	70·0
Substances soluble in water and in caustic potash	12·5	13·0	17·6
Ash	1·6	1·1	1·5

Composition of the Ash in 100 *parts.*

	K^2O	Na^2O	CaO	MgO	Al^2O^3	Fe^2O^3	SiO^2	SO^3	P^2O^5	Cl
Sc. succisa .	38·1	4·9	31·2	4·7	0·2	. .	3·1	5·4	10·4	1·8
Sc. arvensis .	40·7	1·0	29·4	7·0	1·0	0·9	13·2	1·9	1·2	3·5
Sc. columbaria	38·7	1·3	38·1	5·6	0·6	. .	6·0	2·9	4·0	2·6

SCALES OF FISHES AND AMPHIBIA. The chemical composition of the scales of fishes is similar to that of bone, but they contain a larger proportion of organic matter. The organic constituent has, according to Frémy, the same composition as ossein, and is likewise converted into gelatin by boiling with water. The following table exhibits the composition of fish-scales as determined by Chevreul:—

	Lepisostea.	*Perca labrax.*	*Chetodon.*
Animal matter	41·16	55·00	51·42
Basic calcic phosphate . .	46·20	37·80	42·00
Calcic carbonate . . .	10·00	3·06	3·68
Magnesic phosphate . .	2·20	0·90	0·90
Fat	0·40	0·40	1·00
Sodic carbonate . . .	0·10	0·90	1·00
Loss	. .	1·94	

The ash of fish-scales has been analysed by Frémy with the following results:—

	Ash per cent.	Basic calcic phosphate.	Magnesic phosphate.	Calcic carbonate.
Scales of Lepisostea . .	59·3	51·8	7·6	4·0
„ Umber-fish . .	41·9	36·4	0·7	2·0
„ Pike	43·4	42·5	trace	1·3
„ Carp	34·2	33·7	. .	1·1

Brummerstädt found in the scales of the carp, 60·352 per cent. cartilaginous substance (chondrin), and 39·468 inorganic matter, consisting of 34·074 calcic phosphate, 3·777 calcic carbonate, 1·060 magnesic carbonate, and 0·557 magnesic phosphate.

The colours of fish-scales appear to be due to interference. The silvery coating of the scales of the bleak (*Cyprinus alburnus*) is used for making artificial pearls. It is separated by agitating the fishes with water, then drenched with ammonia, and the liquid is preserved in a tightly-corked bottle. Part of the silvery substance dissolves in the ammonia, while the rest remains suspended. The liquid thus obtained, called *Essence d'Orient*, is poured into small glass beads, and then poured out again, leaving the inner surface covered with a thin film, which, as the ammonia evaporates, forms a shining pearly coating on the glass. The bead is then filled up with white wax.

The scales of amphibia are histologically similar to epithelial structures, and chemically to horny substance. The shell of the tortoise and other chelonians is of similar nature. The scales of serpents were found by Frémy to yield a small quantity of alkaline ash, and to consist of a substance resembling epidermis. (*Handw. d. Chem.* vii. 381.)

SCAMMONIC ACID. See JALAPIC ACID (iii. 436).

SCAMMONIN. See JALAPIN (iii. 438).

SCAMMONOLIC ACID. See JALAPINOLIC ACID (iii. 440).

SCAMMONY. *Scammonium.*—A purgative gum-resin, produced, according to Guibourt, by two species of *Convolvulus*, viz. *C. Scammonia* (L.) and *C. hirsutus* (Stev.), growing in Syria and Asia Minor. There are two sorts of it, known in commerce as Aleppo and Smyrna scammony. According to other authorities (*Handw. d. Chem.* vii. 275), Aleppo scammony is obtained from *Convolvulus Scammonia*, and perhaps from other species of the same genus, and Smyrna scammony from *Periploca Secamone*, a plant belonging to the apocyanaceous order.[*]

Aleppo scammony is the most esteemed. When of superior quality it forms flat masses, rather light, and somewhat hollow within, dull and blackish-grey on the fractured surfaces; thin fragments appear transparent when examined by a magnifying glass. It is friable, has a powerful odour, and is often covered with a grey powder resulting from the friction of the lumps. Inferior sorts have the form of flat orbicular lumps, compact, heavy, and without internal cavities. The fracture is then black and vitreous, and thin fragments are very transparent. This kind of scammony is also friable, and has an odour like that of the better sort, but fainter.

Smyrna scammony is dull-brown, heavy, not friable, and has a dull vitreous fracture. Its odour is faint but disagreeable.

The composition of commercial scammony is subject to considerable variations. In three specimens of genuine Aleppo scammony, Marquart (Arch. Pharm. vii. 236; x. 124) found 81·25, 78·5, and 77 per cent. resin soluble in alcohol (which is the active principle), the remainder being made up of wax, extractive matters, gum, starch, albumin, fibrin, and inorganic salts. In one specimen, evidently adulterated, the proportion of resin was as low as 8·5 per cent., the remainder being chiefly made up of starch, gum, gluten, and salts. Another specimen, in which the proportion of resin was 32·5

[*] There is also a false or spurious scammony, known as French or Montpellier scammony, which is prepared in the South of France from the expressed juice of an asclepiadaceous plant, *Cynanchum monspeliacum*, and mixed with various resins and other purgative drugs; but it is a dangerous purgative, and should never be used.

per cent., was found to contain 52 per cent. of gypsum. In four specimens of Smyrna scammony, Marquart found 25, 6, 6, and 7 per cent. resin soluble in alcohol (about $\frac{4}{5}$ of it being also soluble in ether), the rest being made up of extractive matter, gum, starch, woody fibre, and inorganic salts.

The chemical constitution of scammony has been further investigated by Keller and by Spirgatis, who agree very nearly in their analytical results, but differ in the formulæ by which they represent them. Spirgatis regards the resin of scammony as identical with that of spurious or fusiform jalap, which is also derived from the root of a convolvulaceous plant, *Convolvulus orizabensis.* Keller regards the two resins as very closely allied, but not as absolutely identical. (See JALAPIC ACID, JALAPIN, &c., iii. 436—442.)

SCAPOLITE. *Wernerite:* including *Paranthine, Ekebergite, Nuttalite, Tetraclasite, Glaucolite, Atheriastite, Terenite, Porcelain-spar, Stroganowite.*—A silicate of aluminium and calcium (the calcium being, however, more or less replaced by sodium, potassium, and magnesium), occurring in dimetric crystals of the same form as mejonite (iii. 865). Observed faces, oP, $\infty P\infty$, ∞P, P, $P\infty$, $\infty P2$, $\infty P3$. Length of principal axis = 0·4398. Angle $oP : P\infty = 156° 14\frac{1}{2}'$. Cleavage parallel to $\infty P\infty$ and ∞P rather distinct but interrupted. The minerals occur also massive, granular, or with a faint fibrous appearance, sometimes columnar, but most frequently in distinct crystals, occasionally of large size.

Hardness = 5 to 5·5; in a subtranslucent variety from Gouverneur, New York, it is nearly 6. Specific gravity = 2·612 to 2·749. Lustre vitreous to pearly, externally inclining to resinous; on the cleavage and cross-fracture, vitreous. Colour white, grey, blue, green, and red, usually light; streak uncoloured. Transparent to faintly subtranslucent. Fracture subconchoïdal. Brittle. Before the blowpipe it turns white, and melts with tumefaction to a blistered glass. It colours the flame yellow, and when heated in an open tube gives a faint reaction of fluorine. It is completely decomposed by hydrochloric acid without gelatinising.

The numerous analyses which have been made of scapolite exhibit considerable diversities of composition. The silica varies from 42 to above 60 per cent.; the greater number of the analyses, however, give 45, 50, or 60 per cent. The lime varies from 20 to about 3 per cent., those scapolites which are poorest in silica being richest in lime. These latter contain either no other strong base, or only small quantities of alkali, chiefly soda; but as the amount of lime diminishes, that of soda (also of potash) increases for the most part; in that case also magnesia is almost always present, though in small quantity. Lastly, nearly all scapolites contain water, generally less than 1 per cent., but sometimes more than 2 per cent. (For the individual analyses, see *Rammelsberg's Mineralchemie*, pp. 717—720). The oxygen-ratio of the protoxides, sesquioxides, and silica in scapolite, varies:

$$\text{from}\quad \overset{\mathrm{RO}}{1} : \overset{\mathrm{R^2O^3}}{1{\cdot}68} : \overset{\mathrm{SiO^2}}{3{\cdot}16} \quad\text{to}\quad \overset{\mathrm{RO}}{1} : \overset{\mathrm{R^2O^3}}{4{\cdot}47} : \overset{\mathrm{SiO^2}}{8{\cdot}83}$$

Most scapolites exhibit signs of decomposition, indicated by differences of specific gravity, transparency, and hardness, and by the presence of water. The least altered are those which contain the largest proportion of lime. Such are those having nearly the composition of mejonite, $3(2\mathrm{Ca''O.SiO^2}).2(2\overset{\prime\prime\prime}{\mathrm{Al}}{}^2\mathrm{O^3.3SiO^2})$, which in fact is regarded by Rammelsberg, Bischof, and G. Rose as the original scapolite. Among the least altered scapolites are nuttalite from Bolton, Massachusetts, a specimen of which, analysed by v. Rath, gave 44·40 per cent. $\mathrm{SiO^2}$, 25·52 $\mathrm{Al^2O^3}$, 3·79 $\mathrm{Fe^2O^3}$, 20·18 CaO, 1·01 MgO, 2·99 $\mathrm{Na^2O}$, 0·51 $\mathrm{K^2O}$, and 1·24 water (= 98·74), and certain scapolites from Arendal in Norway, and from Malsjö in Wermland, Sweden.

The name *scapolite* (or *wernerite*) includes the common greyish and white varieties of the mineral. *Nuttalite* is bluish, greyish, and dark-greenish. *Paranthine* includes certain compact varieties and crystals of white and pale-blue colour. *Ekebergite* (containing 51·02 per cent. silica, 26·87 alumina, 2·73 ferric oxide, 13·29 lime, and 4·64 soda, besides small quantities of manganous oxide, magnesia, and potash) is massive and subfibrous. The distinctions between these varieties are, however, not very well defined. *Porcelain-spar*, from Passau, is sometimes referred to labradorite: but its analyses give essentially the same oxygen-ratio as scapolite (49·20—50·29 $\mathrm{SiO^2}$, 27·30—27·90 $\mathrm{Al^2O^3}$, 13·53—15·48 CaO, 4·53—5·92 $\mathrm{Na^2O}$, with small quantities of potash and water). *Glaucolite*, which has a lavender-blue or greenish colour, and specific gravity = 2·72—2·9, and has nearly the composition of labradorite (iii. 450), is referred to scapolite by G. Rose, as its cleavages are those of the latter and not of labradorite, and its oxygen-ratio is included within the limits of scapolite.

The alterations of scapolite appear to be chiefly due to the action of carbonated waters, the carbonic acid taking up the lime. *Stroganowite*, from near the Sludänka river, in

Dauria, affords an example of this alteration, containing 40·58 per cent. SiO^2, 28·57 Al^2O^3, 11·05 CaO, 3·50 Na^2O, 0·89 FeO, and MnO, and 14·55 $CaCO^3$. Sometimes the action of the carbonic acid goes so far as to carry off nearly all the stronger bases, and reduce the mineral to a kaolin. Acid carbonate of magnesium in solution converts scapolite into soapstone. By alkaline carbonates in solution, alkalis may be introduced and lime removed, thus forming mica, algerite (i. 113), and perhaps also zeolites. By means of ferrous carbonate dissolved in carbonic acid, an oxide of iron may be introduced; and the iron being oxidised to ferric oxide during the process, epidote in the form of scapolite is produced. *Atheriastite*, a highly hydrated scapolite from Arendal (i. 430), is, according to Hausmann, the original wernerite of Haüy.

Scapolite is usually found in crystalline rocks and in granular limestones, most commonly near its junction with granite, also in beds of magnetic iron accompanying this rock. In the latter situation it occurs at Arendal in Norway and Wermland in Sweden; also in fine crystallisations in Pargas in Finland, &c. Paranthine occurs in the limestone quarries at Marlsjö in Wermland; porcelain-spar in granular limestone at Obernzell, in Bavaria; glaucolite near Lake Baikal in Siberia, in veins in granite. (Dana, ii. 202). The localities of other varieties have already been mentioned.

SCARBROITE. An argillaceous mineral from Scarborough, containing, according to Vernon (Berz. Jahresb. x. 169), 10·5 per cent. silica, 42·5 alumina, 0·25 ferric oxide, and 46·75 water.

SCHABASITE. Syn. with CHABAZITE (i. 843).

SCHAPBACHITE. Syn. with BISMUTH-SILVER (i. 597).

SCHEELE'S GREEN. Arsenite of copper (i. 376).

SCHEELETINE. Native tungstate of lead. (See TUNGSTATES.)

SCHEELITE. Native tungstate of calcium. (See TUNGSTATES.)

SCHEERERITE. This name has been applied to two fossil resins occurring at Uznach, near St. Gallen, in Switzerland: 1. A crystalline resin polymeric with marsh-gas, of specific gravity 0·65, and melting at 44°.—2. A hydrocarbon, polymeric with benzene, already described as retene (p. 97).

SCHEFFERITE. A mineral formerly regarded as a garnet, occurring in the iron mine of Langbanshyttan in Sweden. It has a red-brown colour; hardness = 5·6; specific gravity = 3·39; is slightly attacked by hydrochloric acid, with evolution of chlorine. Contains, according to Michaelson (Jahresb. 1863, p. 804), 52·31 per cent. silica, 19·09 lime, 10·86 magnesia, 10·46 manganous oxide, 1·63 ferrous oxide, and 3·97 ferric oxide (loss by ignition 0·60). The oxygen-ratio of the protoxides and silica is 1 : 2; hence Michaelson regards the mineral as an augite.

SCHLERETINITE. A fossil resin from the coal-mines of Wigan, in Lancashire. It forms black drops and granules, sometimes as big as nuts, brittle, and of conchoïdal fracture. Specific gravity = 1·136. Combustible. By dry distillation it yields water and a large quantity of empyreumatic oil, and leaves a residue of charcoal. It is insoluble in water, alcohol, ether, and alkalis, and is slowly decomposed by strong nitric acid. When it is reduced to fine powder and boiled with water, alcohol, and ether in succession, traces of oil are dissolved, after which it contains at 120°, on the average, 3·68 per cent. of ash, 76·95 per cent. C, 8·95 H, and 10·42 O, corresponding to the formula $C^{20}H^{28}O^2$ (Mallet, Phil. Mag. [4] iv. 261).—This body was erroneously regarded by Dana and Mallet as identical with Rochleder's pyroretin. (Kenngott.)

SCHNEIDERITE. A zeolite from the gabbro of Tuscany, having a confusedly lamino-radiate structure; hardness = 3; white and opaque. Contains, according to Bechi (Sill. Am. J. [2] xiv. 64), 47·79 per cent. silica, 19·38 alumina, 16·76 lime, 11·04 magnesia, 1·62 alkali, and 3·41 water. Breithaupt regards it as a decomposed laumontite.

SCHORLAMITE, or **SCHORLOMITE.** A calcio-ferric silico-titanate occurring on the Ozark Mountains, Magnet Cove, Arkansas, together with elæolite, brookite, and garnet; also embedded in phenolite at Oberschaffhausen, on the Kaiserstuhl. Hardness = 7·75. Specific gravity = 3·783—3·862. It is massive without cleavage, black and opaque, with semivitreous lustre. Before the blowpipe it melts with difficulty on the edges to a black vitreous mass, and exhibits with borax and phosphorus-salt the reactions of titanium. Acids decompose it imperfectly, with separation of gelatinous silica. (Shepherd, Sill. Am. J. [2] ii. 251.—Whitney, Journ. Bost. Nat. Hist. Soc. 1849, vi. 46.)

Analyses.—*a.* From Arkansas (Rammelsberg, *Mineralchemie*, p. 886).—*b.* From the Kaiserstuhl: specific gravity = 3·745 (A. Claus, Ann. Ch. Pharm. cxxix. 213):

	SiO^2	TiO^2	Fe^2O^3	FeO	CaO	MgO	K^2O Na^2O		
a.	26·24	21·34	20·11	1·57	29·38	1·36	. .	=	100
b.	29·55	21·18	18·08	. .	25·13	1·22	4·22	=	99·38

Rammelsberg deduces from his analysis, which agrees very nearly with those of Whitney and Crossley, the formula $3(2Ca''O.SiO^2).(2Fe^2O^3.3SiO^2).(2Ca''O.3TiO^2)$.

SCHORLITE. Syn. with Topaz.

SCHORLOMITE. Syn. with Schorlamite.

SCHREIBERSITE. A phosphide of iron and nickel, occurring in meteoric iron, and forming the principal part of the residue left on dissolving the iron in hydrochloric acid (Meteorites, iii. 978). Under the microscope it often appears in sharply-defined crystals. Its colour is sometimes steel-grey, sometimes yellowish or brownish. It is strongly magnetic, dissolves with difficulty in acids, and is often mixed with graphite and silica. Hardness = about 6·5. Specific gravity = 7·01—7·22. It varies greatly in composition, as the following analyses will show (*Rammelsberg's Mineralchemie*, p. 947):—

	Elbogen.	*Bohumilitz.*	*Braunau.*	*Seeläsgen.*	*Schwetz.*	*Arva.*	
	Berzelius.		Duflos. Fischer.	Rammelsberg.		Patera.	Bergemann.
Phosphorus . .	14·17	14·76	12·72	7·37	36·00	7·26	6·14
Iron	68·11	69·45	60·13	62·63	22·34	87·20	78·36
Nickel	17·72*	15·79	27·15	29·18	36·66	4·24	15·47
	100.00	100.00	100.00	Ca0·82	5·00	98·70	99·97
				100·00	100·00		

	Krasnojarsk.	*Zacatecas.*		*Ocotillan.*	*Misteca.*	*Cosbee's Creek.*	*Knoxville.*
	Berzelius.	Bergemann.	H. Müller.		Bergemann.		Smith.
Phosphorus	18·47	24	10·23	3·54	11·61	3·31	14·39
Iron . . .	48·67	76	75·02	86·32	58·36	87·77	56·60
Nickel . .	18·33		14·52	10·14	29·95	8·92	26·76
Magnesium	9·66	100	99·77	100·00	99.92	100·00	Co 0·34
	95·13						98·09

Faye (Compt. rend. lvii. 801), by exposing a mixture of 8 grms. ferric oxide, 3·7 grms. nickel-oxide, 10·1 sodic phosphate, 6 grms. silica, and 2 grms. charcoal, to a white heat in a graphite crucible, obtained a black slag, a metallic regulus of nickel and iron, and between the two a crust of yellowish metallic shining laminæ, exhibiting the characters of schreibersite.

SCHRÖTTERITE. An amorphous mineral, resembling allophane, from the Döllinger mountain, near Frankenstein in Styria, where it occurs in nests between clay-slate and granular limestone. Hardness = 3—3·5; specific gravity = 1·95—2·05. Colour greenish, yellowish, or sometimes spotted with brown. Contains, according to Schrötter (J. pr. Chem. xi. 380), 11·94 per cent. silica, 46·29 alumina, 2·80 ferric oxide, 1·16 lime, 0·25 cupric oxide, 0·63 sulphuric acid, and 35·85 water, which may be represented by the formula $5Al^2O^3.2SiO^2.20H^2O$. It is probably a mixture containing hydrate of aluminium.

SCHULZITE. Syn. with Cœlestin (i. 1069).

SCILLA MARITIMA. *Squill.* A liliaceous plant, growing wild on the shores of the Mediterranean. The fleshy bulbs, which are used in medicine, have been investigated by several chemists, but with somewhat discordant results. They contain a volatile oil, an acrid substance, a bitter principle, gum, sugar, and, according to Landerer, starch and fat, together with phosphate, citrate, and perhaps also tartrate of calcium.

The volatile oil, obtained by distilling the bulbs with water, is mobile, slightly coloured, has a pungent disagreeable odour (like that of garlic or mustard oil), and blisters the skin; so likewise does its alcoholic solution.

The investigations on scillitin, the active ingredient of the bulbs, have not determined whether it is to be classed with the resins, the alkaloïds, or the bitter principles. Mandet (Compt. rend. li. 87) distinguishes two peculiar bodies, the poisonous and irritating sculeïn, and the non-poisonous scillitin, but adds nothing further concerning them. Schroff (N. Repert. xiv. 241) also distinguishes a narcotic principle (*scillitin*) and an acrid non-volatile principle. Righini (Repert. lxiii. 87) regards scillitin as impure veratrin.

a. According to Tilloy (J. Pharm. xii. 635; *ibid.* [3] xxiii. 406), squill contains no volatile acrid principle, but crystals of calcic citrate [oxalate (Schroff)] which irritate and inflame the skin when rubbed upon it. The active constituents are an acrid resin and a bitter substance.

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* With Magnesium.

Dried squill-powder gives up to ether an agreeably-smelling yellow fat (or fatty acid?) which may be freed from adhering bitter substance by means of hot water. When the powder which has been exhausted with ether is digested with alcohol, a very acrid and bitter tincture is obtained, leaving on evaporation an acrid resin, which is freed from adhering fat by ether, and from sugar by water. This resin is very poisonous; it softens in hot water, dissolves in alkalis and alcohol, and is not altered by acids.—The bitter substance is extracted by hot water from squill previously treated with ether and alcohol; it is precipitated from the liquid by charcoal, which gives it up again to boiling alcohol (Tilloy).

b. Vogel (Schw. J. vi. 101) and Lebourdais (Ann. Ch. Phys. [3] xxiv. 62) prepare the bitter substance as follows:—

1. Vogel exhausts the concentrated juice with alcohol, evaporates the tincture, dissolves the residue in water, precipitates tannic acid by neutral acetate of lead, removes excess of lead by means of sulphydric acid, again filters, and evaporates. There then remains scillitin, together with sugar and salts, in the form of a colourless friable mass, which has a very bitter, afterwards sweetish taste, and causes vomiting and purging. This mass softens quickly in the air, and dissolves easily in water and absolute alcohol, and in vinegar.—2. Lebourdais precipitates the highly coloured and very viscid decoction of squill with neutral acetate of lead, and agitates the cold filtrate with purified animal charcoal till it loses its colour and bitterness. The charcoal is then washed and dried, and boiled with alcohol, which takes up the scillitin, and leaves it behind on evaporation.—Scillitin thus obtained is an amorphous, neutral, non-hygroscopic mass, which decomposes easily when heated, dissolves with purple colour in oil of vitriol, afterwards blackening, and is decomposed by nitric acid.—A portion placed upon the tongue produces the sensation of a caustic.—Bley (N. Br. Arch. lxi. 141) operated in the same way as Lebourdais, avoiding too great heat, and obtained by spontaneous evaporation, long, colourless, flexible needles, having a very bitter taste, becoming amorphous when gently warmed, and not afterwards susceptible of crystallisation.—According to Wittstein (Repert. [3], iv. 200), the bitter of squill is not precipitated by basic acetate of lead, nor by hydrated oxide of lead, which latter, however, precipitates the acrid constituent.

c. Marais (J. Pharm. [3] xxx. 130) and Landerer (Repert. xlvii. 442) believed they had obtained an alkaloïd, which Tilloy was not able to isolate.

1. Marais exhausts either the dried squill with alcohol of 56 per cent., or the fresh bulbs with alcohol of 90 per cent., mixes the tincture with milk of lime, agitates with ether, separates the supernatant layer of liquid, and evaporates, whereupon scillitin and fat remain, the latter of which is removed by again dissolving the residue in alcohol.—The product is an amorphous, hygroscopic, pale-yellow mass, having a pungent bitter taste and an alkaline reaction.—It dissolves in oil of vitriol, forming a violet solution, from which water precipitates green flocks, and in nitric acid with red colour, which quickly disappears; it is insoluble in hydrochloric acid, but soluble in ammonia and caustic alkalis, becoming decomposed and losing its bitter taste. When heated with hydrate of potassium, it evolves ammonia. It does not dissolve in water; produces with ferric chloride an orange-yellow, and with platinic chloride a yellow precipitate, and combines with acetic acid. It dissolves in alcohol and ether. Taken internally, it acts as an emetic and violent purgative, and afterwards as a narcotic. (Marais.)

2. Landerer digests the crushed inner portions of squill with very dilute sulphuric acid, boils down the filtrate to one-half, saturates it with lime, and sets it aside for three days; then collects and dries the residue. When this residue is boiled with alcohol, the filtrate deposits on evaporation a very small quantity of extremely bitter needles, which are insoluble in water, and sparingly soluble in alcohol. The needles have an alkaline reaction and neutralise acids, forming therewith crystallisable salts, which melt when heated (evolving vapours which excite coughing) and carbonise, but do not leave a trace of lime. This body does not appear to be obtained from dried squill.

SCILLITIN. See the last article.

SCIRPUS. The ash of the bulrush (*Scirpus lacustris*) has been analysed by Fleitmann (Ann. Ch. Pharm. lviii. 391) and by Schulz-Fleeth (Pogg. Ann. lxxxiv. 80), with the following results (deducting the charcoal):

K^2O	Na^2O	CaO	MgO	Fe^2O^3	SO^3	SiO^2	CO^2	P^2O^5	$NaCl$	KCl	
15·3	. .	7·3	2·6	1·17	4·8	28·1	. .	9·5	27·3	3·9	= 99·37 (Fleitmann).
9·7	5·0	7·0	2·3	0·24	5·5	46·5	7·9	4·8	10·1	. .	= 99·04 (Schulz-Fleeth).

SCLEROGEN. A term applied to the incrusting matter deposited within the cells of woody fibre, also called *lignin.* This substance is said by Payen to be distinguished from cellulose by assuming an orange colour when treated with potash and iodine, whereas pure cellulose turns blue under the same circumstances. Schleiden, on the other hand, denies its existence as a distinct compound. (See *Gmelin's Handbook*, xv. 124.)

SCOLECITE. *Lime Mesotype, Needlestone, Poonahlite, Fibrous Zeolite:* including *Mesolite* or *Lime* and *Soda Mesotype.*—A hydrated calcio-aluminic silicate, in which the calcium is sometimes partly replaced by sodium. It forms monoclinic crystals, in which the ratio of the axes $a : b : c = 1{\cdot}0282 : 1 : 0{\cdot}6791$. Angle of inclined axes $b, c = 89°6'$. The crystals are prismatic or acicular, consisting of a prism of 91°35′, acuminated by four faces of a monoclinic pyramid composed of the hemipyramid P of 144° 40′ and the hemipyramid —P of 144°20′; they bear a strong general resemblance to the crystals of natrolite, which consists of the orthorhombic prism $\infty P = 91°$, acuminated by four faces of the pyramid P inclined to the lateral edges at angles of 143°20′ and 142°40′. Twins also occur parallel to the orthodiagonal. Cleavage nearly perfect, parallel to ∞P. The mineral likewise occurs fibrous, massive, and radiated. Hardness = 5—5·5. Specific gravity = 2·2—2·7. Lustre vitreous, or silky when fibrous. Transparent to subtranslucent. Pyrolectric. Before the blowpipe it curls up like a worm (hence the name, from σκώληξ, a worm), and finally melts to a bulky shining slag, which in the inner flame becomes a vesicular slightly shining bead.

A. Scolecite or Lime Mesotype.—*Analyses*: *a.* From the Berufiord, Iceland (Gibbs, Pogg. Ann. lxxi. 565).—*b.* Faröe Islands (Stephan, *Rammelsberg's Mineralchemie*, p. 795).—*c.* Staffa: fibrous (Fuchs and Gehlen, Schw. J. viii. 353; xviii. 1).—*d.* Isle of Mull: radiate, accompanied by epidote (Scott, Edin. N. Phil. J. Oct. 1852).—*e.* Auvergne (Guillemin, Ann. Min. xii. 8).—*f.* Niederkirchen, in Rhenish Bavaria (Riegel, Jahrb. pr. Pharm. xiii. 1).—*g.* East Indies: spherical aggregates having a radiate structure (Taylor, J. pr. Chem. lxiii. 467).—*h.* Cachapual Valley, in Chili; in porphyry (Domeyko, Ann. Min. [4], ix. 3):—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Silica	46·72	45·82	46·75	46·21	49·0	48·08	46·87	46·3
Alumina . . .	25·90	26·28	24·82	27·00	26·5	23·93	25·32	26·9
Lime	13·71	13·59	14·20	13·45	15·3	14·22	13·80	13·4
Soda	. .	1·10	0·39	. .	. .	0·32	0·45	
Potash	. .	. .	. .	. .	. .	. .	0·13	
Water	13·67	13·60	13·64	13·78	9·0	13·55	13·46	14·0
	100·00	100·39	99·80	100·44	99·8	100·10	100·03	100·6

These analyses lead to the formula $(Ca''O.SiO^2).(\overset{\prime\prime}{Al}{}^2O^3.2SiO^2).3H^2O$.

B. Mesolite or Lime and Soda Mesotype.—*a.* Portrush, Ireland (also called *Harringtonite*), Thomson (*Outlines of Mineralogy*, i. 428).—*b.* Kilmore in the Hebrides (Heddle, Phil. Mag. [3] xi. 273).—*c.* Berufiord, Iceland: spherical radiate (Waltershausen, *Vulk. Gesteine*, p. 267).—*d.* Ireland: *Antrimolite* (Heddle, *loc. cit.*).—*e.* Faröe Islands (Berzelius, Jahresbericht, iii. 147).—*f.* Tyrol: massive and fibrous (Fuchs and Gehlen, Schw. J. viii. 353; xviii. 1).—*g.* Iceland: excentrically fibrous (Breidenstein, *Rammelsberg's Mineralchemie*, p. 798).—*h.* Talisker in Skye (Heddle):—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Silica . .	44·84	46·26	46·41	47·07	46·80	46·04	45·78	46·71
Alumina .	28·48	26·48	26·24	26·23	26·50	27·00	27·53	26·62
Lime . .	10·68	10·00	9·68	9·88	9·87	9·61	9·00	9·08
Soda . .	5·56	4·98	4·87	4·88	5·40	5·20	5·34	5·39
Water . .	10·28	13·04	13·75	12·24	12·30	12·36	12·38	12·83
	99·84	100·76	100·95	100·30	100·87	100·21	100·03	100·63

Rammelsberg represents the analyses *b, c, d* by the formula:

$$3[(Na^2O.SiO^2).(Al^2O^3.2SiO^2).2H^2O] + 7[(Ca''O.SiO^2).(Al^2O^3.2SiO^2).3H^2O]$$

and the rest by the formula:

$$[(Na^2O.SiO^2).(Al^2O^3.2SiO^2).2H^2O] + 2[(Ca''O.SiO^2).(Al^2O^3.3SiO^2).3H^2O].$$

These two formulæ, however, give very nearly the same percentage composition, the first requiring 46·92 SiO^2, 26·05 Al^2O^3, 9·95 CaO, 4·75 Na^2O, and 12·33 H^2O; the second, 46·96 SiO^2, 26·09 Al^2O^3, 9·48 CaO, 5·28 Na^2O, and 12·19 H^2O.

Scolecite occurs also in Greenland, at Pargas in Finland, in Auvergne, and in veins in the Kilpatrick Hills.

Poonahlite, a variety from Poonah in Hindostan, has the angle $\infty P : \infty P = 91° 49'$ (Kenngott). Gmelin (Pogg. Ann. xlix. 428) found it to contain 45·12 per cent. silica, 30·44 alumina, 10·20 lime, 0·66 soda (with a trace of potash), and 13·89 water (= 99·81).

Antrimolite occurs in white fibrous stalactites at Antrim, four miles east of the Giant's Causeway. Angle of prism = 92° 13'; outer edges bevelled by a prism of 150° 30'. Hardness = 3·75. Specific gravity = 2·096.

SCOLEXEROSE. A mineral from Pargas in Finland, regarded by Nordenskiold as a variety of labradorite (iii. 451), by others as a scapolite.

SCOPARIN. $C^{21}H^{22}O^{10}$. (Stenhouse, Phil. Trans. 1851, p. 422; Ann. Ch. Pharm. lxxviii. 15.)—A substance contained in *Spartium Scoparium*, and apparently constituting the diuretic principle of that plant.

Preparation.—The decoction obtained by boiling the plant for six or eight hours with water, when evaporated to one-tenth of its bulk, and left at rest for 24 hours, solidifies to a jelly, containing scoparin together with chlorophyll and a small quantity of sparteïne. The jelly is washed with a little cold water, dissolved in boiling water containing a few drops of hydrochloric acid, filtered, and set aside till it solidifies; and the jelly again formed is purified by washing, pressing, drying over the water-bath, and dissolving in boiling water, which now leaves most of the chlorophyll undissolved. The chlorophyll may also be precipitated from the aqueous solution by long-continued boiling; it is deposited from a moderately concentrated solution before the scoparin, and may be separated by filtration at the proper point.

Scoparin thus obtained forms, after drying in a vacuum, a pale-yellow, brittle, amorphous mass, tasteless, inodorous, and neutral. By precipitating its cold ammoniacal solution with hydrochloric acid, dissolving the somewhat more solid jelly in boiling water, and cooling slowly, a small quantity of pale-yellow crystalline stars is obtained, together with gelatinous scoparin. The solution in hot alcohol likewise yields a jelly on partial evaporation, and crystals in the cold. When an attempt is made to recrystallise the latter from hot alcohol, there remains a residue which dissolves with difficulty in water and alcohol, and is obtained as a jelly having the original degree of solubility only by dissolving it in ammonia-water, and precipitating with hydrochloric acid. The crystals and the jelly have the same composition when dry.

Scoparin puffs up when *heated*, carbonises without subliming, and burns with bright flame. A solution in *potash* or in *acids* is decomposed by boiling, with formation of a greenish-brown resin.—Scoparin assumes a blue-green colour with *bromine*, and a dark-green with *solution of chloride of lime*.—With *nitric acid* it forms picric acid.

Scoparin is sparingly soluble in cold, more freely soluble in hot water, forming pale-yellow solutions. It dissolves also in cold *alcohol*, more freely in boiling alcohol. It dissolves slightly in strong *acids*; very easily, with deep yellowish-green colour, in *caustic ammonia*, the *fixed alkalis*, and *alkaline carbonates*, less easily in lime- and baryta-water. The ammoniacal solution leaves, on spontaneous evaporation, a green jelly, nearly free from ammonia.

Scoparin throws down greenish-yellow flocks from *neutral* and *basic acetate of lead*. It does not precipitate *mercuric chloride* or *nitrate of silver*.

SCORDEÏN. A yellow aromatic substance obtained from *Teucrium Scordium*. (Winckler, Repert. Pharm. xxviii. 352.)

SCORILITE. A mineral from Juan del Rio Cara del Calvaxio, in Mexico, containing, according to R. Thomson (J. pr. Chem. viii. 506), 58·0 per cent. silica, 16·8 alumina, 13·3 ferrous oxide, 8·6 lime, and 2·0 water. It occurs in brown slag-like masses, with numerous cavities. Streak white. Hardness = 2·0. Specific gravity = 1·70. Before the blowpipe it becomes lighter in colour, but does not fuse. With fluxes it gives the iron reaction.

SCORODITE. *Neoctese. Cupreous Arsenate of Iron.*—A hydrated ferric arsenate occurring in trimetric crystals, which exhibits the combination $\infty\breve{P}\infty \,.\, \infty\bar{P}\infty \,.\, P \,.\, \infty\breve{P}2$, sometimes with ∞P and $\frac{1}{2}P$. Axes $a : b : c = 1 : 1·1511 : 1·0977$. Angle $\infty P : \infty P = 98° 2'$. Cleavage parallel to $\infty\breve{P}2$ imperfect, parallel to $\infty\bar{P}\infty$ and $\infty\breve{P}\infty$ in traces. The crystals are sometimes single, sometimes implanted in groups or grown together in granular aggregates. The mineral also occurs in botryoïdal, kidney-shaped, tubular, and other forms, also as an incrustation (arsenical sinter). Hardness = 3·5—4. Specific gravity = 3·1—3·3. Lustre vitreous, subadamantine, and subresinous. Colour pale leek-green or liver-brown. Streak white. Subtransparent to translucent. Fracture uneven. Before the blowpipe on charcoal it emits an alliaceous odour (hence the name, from σκόροδον, garlic), and fuses to a reddish-brown or black scoria, magnetic after all the arsenic is expelled. The mineral is not acted upon by nitric acid, but dissolves easily in hydrochloric acid.

Analyses:—*a*. Graul, near Schwarzenberg in Saxony (Damour, Ann. Ch. Phys. [3] x. 412).—*b*. Vaubry, Dept. Haute-Vienne: crystallised; specific gravity = 3·11 (Damour).—*c*. Cornwall (Damour).—*d*. Antonio Pereira in Brazil: specific gravity = 3·18 (Berzelius, Jahresbericht, v. 205).—*e*. From the same (Damour).—*f*. Loaysa, near Marmato, New Granada (Boussingault):

	a.	*b*.	*c*.	*d*.	*e*.	*f*.
Arsenic anhydride	52·16	50·95	51·06	50·78	50·96	49·6
Phosphoric „	. .	. .	. .	0·67		
Ferric oxide	33·00	31·89	32·74	34·85	33·20	34·3
Water	15·58	15·64	15·68	15·55	15·70	16·9
	100·74	98·48	99·48	101·85	99·86	100·8

These analyses lead to the formula $Fe^2O^3.As^2O^5.4H^2O$, or $\left.\begin{matrix}As^{v}\\Fe'''\end{matrix}\right\}O^4.2H^2O$, requiring 49·84 As^2O^5, 34·60 Fe^2O^3, and 15·56 water.

An iron sinter from Nertschinsk in Siberia, containing, according to Hermann (J. pr. Chem. xxxiii. 95), 48·05 As^2O^5, 36·41 Fe^2O^3, and 15·54 water, is an amorphous scorodite.

Scorodite occurs altered to limonite.

SCORZA. A variety of epidote.

SCORZONERA. The roots of *Scorzonera hispanica*, a plant belonging to the cichoraceous tribe of *Compositæ*, contain starch. According to Witting (Arch. Pharm. [2] cv. 286), the expressed juice of the plant contains mannite.

SCROPHULARIA. Two species of this genus of plants have been examined chemically by Walz (Jahrb. pr. Pharm. xxvi. 296; xxvii. 12). *S. nodosa* contains a bitter substance called by Walz α-scrophularin, which dissolves very slowly in water, and is precipitated in white flocks by tannin; also a resin insoluble in water, soluble in alcohol and ether.

Sc. aquatica contains a bitter substance, β-scrophularin, differing in taste and solubility from α-scrophularin; an irritating resinous substance, scrophulacrin, soluble in alcohol and ether; and a resinous substance, scrophularesin, soluble in alcohol, insoluble in water and in ether.

100 pts. of *Sc. aquatica* yielded 7·8 pts., and 100 pts. of *Sc. nodosa* 7·5 pts. of ash, composed as follows:—

	K^2O	Na^2O	CaO	MgO	Fe^2O^3	NaCl	SO^3	P^2O^5	CO^2	SiO^2	Charcoal and sand		
Sc. aquatica	2·3	. .	15·2	5·8	1·3	24·3	4·1	25·3	8·0	7·0	7·0	=	100·3
Sc. nodosa	4·4	13·1	25·5	13·1	1·0	6·2	3·1	13·0	15·2	4·5	0·8	=	99·9

SCURVY-GRASS. See COCHLEARIA (i. 1062).

SCUTTELLARIN. A bitter substance contained in *Scutellaria laterifolia*. (Cadot de Gassicourt, J. Pharm. v. 432.)

SCYLLITE. A neutral substance occurring in cartilaginous fishes, chiefly in the kidneys of the sharks and rays, in the milt and liver of the former, and in the liver and gills of the latter. It does not contain either nitrogen or sulphur, and is probably isomeric with inosite; but its composition has not been exactly determined.

To prepare it, the organs just mentioned are triturated with pounded glass, then stirred up repeatedly with alcohol, and pressed; the filtered extracts are evaporated; the residue is exhausted with water; and the filtrate is again evaporated. The syrupy residue is then treated with absolute alcohol; the portion insoluble therein is dissolved in water; and the solution is left to evaporate, whereupon it deposits crystals of taurine and scyllite. These crystals are separated from the mother-liquor by filtration, then dissolved; and the somewhat concentrated solution is treated with basic acetate of lead, whereby a lead-compound of scyllite is precipitated, from which the lead may be separated by sulphydric acid.

Scyllite crystallises in anhydrous monoclinic prisms having a vitreous lustre, less soluble in water than inosite, insoluble in absolute alcohol. It has a faint sweetish taste, and is precipitated by basic acetate of lead, from its perfectly neutral aqueous solution, in a pasty form, like inosite. It does not, however, exhibit the reactions of inosite with nitric acid, ammonia, or chloride of calcium. Nitric acid, of specific gravity 1·3, dissolves it only at the boiling heat, and even then but slowly, and without evolution of gas. The solution contains unaltered scyllite, which may be separated by alcohol. Scyllite is dissolved by strong sulphuric acid also, only at high temperatures;

it is not coloured by boiling with strong soda-ley, and does not reduce an alkaline cupric solution. (Frerichs and Städeler, J. pr. Chem. lxxiii. 48.)

SEA-SALT. Chloride of sodium more or less mixed with other salts, obtained by evaporation of sea-water. (See SODIUM, CHLORIDE OF.)

SEA-WATER. See WATER.

SEAWEEDS. These plants, which occur abundantly in the open sea, and are often heaped up in vast quantities on the shore, are used for various purposes—viz., as food and medicine, in certain manufactures, but more extensively as manure, and for the sake of their ash (called kelp or varee), which is valuable as a source of potassium-salts, and as the principal source of iodine.

1. *Seaweed as Food and Medicine.*—Many seaweeds contain large proportions of gelatinous or mucilaginous matter, and afford demulcent and nutritive jellies; the proportion of nitrogen in them is also very considerable. The following table exhibits the proportions of dry matter and nitrogen contained in some of the species most used, as food for men or as fodder for cattle, in the British Islands and the North of Europe, according to the determinations of J. Davy and Apjohn:—

Percentage of Dry matter and Nitrogen in Seaweed.

Plants.	Water.	Dry matter.	Nitrogen per cent. in dry matter.
Chondrus crispus (Carragheen or Irish moss), bleached	17·92	82·08	1·534
„ „ „ unbleached.	21·47	78·53	2·142
Gigartina mammillosa	21·55	78·45	2·198
Laminaria digitata, or dulse tangle	21·38	78·62	1·588
„ black tangle	31·05	68·95	1·396
Rhodomenia palmata, or dylisk	16·56	83·44	3·465
Porphyra laciniata, or laver	17·41	82·59	4·650
Iridæa edulis	19·61	80·39	3·088
Alaria esculenta, or murlins	17·91	82·09	2·424

The proportion of nitrogen in these plants appears, from these analyses, to be larger than in most other vegetable esculents: the best wheat-flour (dried at 100°) containing, according to Apjohn, 1·817 per cent. nitrogen, potatoes 0·541, beetroot 1·848, mangolds 1·781, and Swedish turnips 1·843. This large proportion of nitrogen has been supposed to account for the high nutritive value attributed to many kinds of seaweed; but the mere percentage of nitrogen existing in a substance cannot be taken as a certain indication of its nutritive value, as the form in which the nitrogen exists is likewise of great importance in determining whether the nitrogenous constituent of the plant is capable of ready assimilation in the body of an animal: moreover, the nutritive power of a substance cannot be determined without taking account also of its non-nitrogenous constituents.

The use of seaweed as food is most extensive in China and Japan. *Laminaria saccharina*, sweet tangle or sea-tape, highly esteemed in these countries, has been found by Stenhouse to contain large quantities of mannite.

Plocaria candida (called *Agar-Agar* by the Malays, and *Bulung* in Java) is imported into this country as commercial Ceylon Moss. It is a small delicate white fucus, containing about 70 per cent. of starch and vegetable jelly. The edible birds'-nests, esteemed as a delicacy in China, are probably constructed from this plant by a species of swallow, the *Hirundo esculenta.*—*Gelidium corneum* is the *algue de Java*, which is made into an iced jelly, and sold in Ningpo under the name of *Nin-mau* (ox-hair vegetable). Payen has extracted from it 27 per cent. of a peculiar vegetable substance, called gelose, which he finds to possess ten times the gelatinising power of the best isinglass. The same substance is obtained from *Plocaria lichenoïdes*, a seaweed from the Mauritius, and in small quantity from several European seaweeds; it is said also to be obtained from certain lichens growing on trees in the South of China, and in the southern islands of the Philippine Archipelago (ii. 829).—*Fucus saccharinus*, the *Kambon* of the Japanese and the *Sea-cabbage* of the Russians, which is found in great abundance on the islands and shores of Eastern Asia, is used as an ingredient of soap, and eaten with fish, or boiled and eaten merely with salt. *Laminaria potatorum* furnishes the natives of Australia with food, and serves also as a material for their tools and vessels; other species of the same genus constitute an important resource to the poor on the west coast of South America, to the Fuegians, and the inhabitants of the country near the Straits of Magellan. Under the name of *bull-kelp*, it is largely eaten in New Zealand and Tasmania.—*Durvillia utilis* is used as food in Valparaiso, and by the poorer inhabitants of the west coast of South America.—*Eucheuma speciosum* and *Gigartina speciosa* are eaten in Australia.

The use of seaweed as medicine depends partly on the gelatinous matter, partly on the iodine contained in it. Carragheen moss has been found useful in pulmonary complaints.—*Fucus vesiculosus*, bladder-wraïk or lady-wrack, is used externally as a friction in glandular enlargements, and the juice has been given internally with advantage for the same purpose.—*Sargassum bacciferum* is the celebrated gulf-weed of the Atlantic, the stems of which are said to constitute the *gôîtresticks* chewed in South America, where that disease is prevalent, but they more probably come from the stems of the *Laminaria digitata*.—*Plocaria helminthocortos* (also called *Gracilaria lichenoïdes* or *Sphærococcus*, *Gigartina lichenoïdes*, and Corsican moss) has long been used by the Corsicans as an anthelmintic.

2. *Use in Manufactures.*—A process has been recommended by Dr. Stenhouse for the manufacture of acetic acid from seaweeds by fermentation. His experiments were conducted with some of the fuci; these were mixed with lime, and kept moist at a temperature of 90° F. He obtained by distillation with sulphuric acid, an average of 1·5 per cent. of anhydrous acetic acid, contaminated with butyric acid. This might, however, be separated and turned to account in the manufacture of butyric ether or essence of pine-apple. The best method would be to ferment the plants in pits with lime or chalk, at the ordinary temperature in the summer, leaving each portion in for two or three months, and supplying its place by a fresh load until the lime was saturated; the liquid would then be pumped out, evaporated to dryness, the residue sold as crude acetate of calcium, and the weed carried to the manure-heap. The whole process might be roughly and economically carried on by an agriculturist near the sea.

Seaweeds are used as substitutes for horn, shell, whalebone, indurated leather, &c., in the manufacture of various articles. One process consists in immersing the weed, from which all extraneous matters have previously been removed, in a lye of caustic lime for three hours, then steeping it in very dilute sulphuric acid, and afterwards in a solution of common salt, after which it may be moulded into any desired form. Or the dry material is ground to powder and mixed with glue, to which some alum and powdered resin are added, or with coal-tar or bitumen, and baked, then rolled out, or pressed in moulds. The stems of *Laminaria digitata* (tangle or sea-girdle) make excellent handles for knives, files, &c. If the blade is inserted when the stem is fresh cut, and the weed then allowed to dry, it contracts, holding the blade firmly, and presenting a brown wrinkled appearance, somewhat like buck-horn.

A kind of soap may be made by treating some of the common seaweeds with alkalis.

Attempts have been made to use seaweeds in the manufacture of paper, and for the production of textile fabrics; but the true algæ are not adapted for this purpose, as they are destitute of fibrous structure. The seawrack, *Zostera marina*, which is not an alga, but contains fibre resembling that of the grasses, promises better results when used for such purposes.

Many seaweeds exhibit very brilliant colours, but it does not appear that any attempts have hitherto been made to utilise them. Several varieties of *Griffithsia* yield to pure water a brilliant crimson colour, which is precipitated by soluble chlorides, and appears to combine with alumina and other metallic oxides.

3. *Seaweed as Manure.*—The value of seaweed as manure is most appreciated in the Channel Islands; the "varec" or "vraic," as the weed is there called, is considered so valuable that special laws are enforced for its regular collection and fair distribution amongst the agriculturists, many of whom use no other manure. "Point de vraic, point de hangard" has passed into a local proverb. The weed is either thickly spread on the land, and ploughed in fresh with a deep plough, or dried on the beach, and burnt on the cottagers' hearths as fuel; the charred ash thus produced sells at 6*d*. per bushel for manure. "Driftweed" is also largely used in Ireland, as the only manure for the potato crop; this is interesting, because the potato requires a considerable supply of potash. This alkali can hardly, however, be required in the Channel Islands, as the granitic subsoil would, in disintegration, furnish it in abundance; it is probably the earthy phosphates that render the weed so fertilising there. This is borne out by the fact that the lixiviated seaweed ash, from which the alkalis have been removed, meets with a ready sale in Guernsey, and is esteemed indeed richer, no doubt on account of the increased percentage of phosphates. The residual seaweed ash from the iodine factories in France is highly valued as a manure, and carried for that purpose a distance of thirty miles from the factory.

Seaweed is also much used as manure in the Hebrides, the Isle of Thanet, Cornwall, and the Isle of Man.

100 pts. of decomposed and dried seaweed contain, according to Way, 65·62 per cent. organic matter, 13·65 soda, 16·00 soluble salts, and 3·23 nitrogen (= 4 of ammonia).

4. *For the production of Kelp or Varec, as sources of Iodine and Potassium-salts.*—This part of the subject has already been treated under the head of "POTASSIUM-SALTS, MANUFACTURE OF" (iv. 714). We here give a table of the composition of the ash of several kinds of seaweed, as determined by Schwitzer, Forchhammer, and Godecheus:—

Ash of Seaweed.

Constituents of the Ash.	*Laminaria saccharina,* North Sea.	*Fucus serratus,* North Sea.	*Laminaria latifolia,* Hoffmansgave.	*Furcellaria fastigiata,* Cattegat.	*Chondrus crispus,* Cattegat.	*Iridaea edulis,* Cattegat.	*Polysiphonia elongata,* Hoffmansgave.	*Delesseria sanguinea,* Cattegat.	*Fucus digitatus,* from the mouths of the Clyde.	*Fucus nodosus,* from the mouths of the Clyde.	*Fucus serratus,* from the mouths of the Clyde.
Potash	24·77	16·02	16·91	21·36	18·00	23·42	21·23	13·72	22·40	10·07	4·51
Soda	1·84	6·01	. .	24·77	19·47	16·06	5·06	21·34	8·29	15·80	21·15
Lime	6·50	7·05	8·28	6·02	7·11	10·23	2·92	2·30	8·79	10·98	11·09
Magnesia	8·13	7·59	6·80	11·04	11·80	. .	20·56	5·94	7·44	10·93	11·66
Chloride of sodium . .	33·72	38·72	26·92	. .	. .	1·66	13·85	. .	28·39	20·16	18·76
" potassium .	. .	. .	10·18								
Iodide of sodium . .	4·70	0·27	. .	. .	. .	. .	. .	. .	3·62	0·54	1·33
Phosphate of calcium .	8·41	4·95	12·80	3·96	0·76	23·23	2·99	3·90	5·63	3·34	9·67
" iron . .	0·75	0·64									
Oxide of iron	. .	. .	. .	. .	. .	. .	. .	. .	0·62	0·29	0·34
" manganese . .	. .	. .	. .	0·22							
Sulphuric acid . . .	10·60	18·35	12·63	32·63	42·86	25·19	28·66	40·42	13·26	26·69	21·06
Silica	0·58	0·40	0·69	. .	. .	. .	2·83	12·38	1·56	1·20	0·43
	100·00	100·00	95·21	100·00	100·00	99·79	98·10	100·00	100·00	100·00	100·00
Percentage of ash in weed dried at 100° . . .	97·8	25·83	13·62	18·92	20·61	9·86	17·10	13·17	20·40	16·19	15·63
	Schwitzer.		Forchhammer.						Godecheus.		

The high temperature to which the seaweed is exposed in the ordinary process of incineration gives rise to the loss by volatilisation of at least half of the iodine, and of a certain portion of the potassium-salts, and likewise enables the carbon to reduce the sulphates to sulphites, hyposulphites, and sulphites, which accumulate in the mother-liquors, and necessitate the consumption of a large quantity of sulphuric acid to reconvert them into sulphates.

To obviate these and other disadvantages attending the ordinary process, and further to economise the products, Mr. E. C. Stanford proposes to subject the seaweed, previously dried, to destructive distillation in iron retorts, whereby they yield the usual products of the dry distillation of organic bodies—such as hydrocarbons, naphtha, ammonia, acetic acid, and illuminating gas. The residual charcoal then yields, on lixiviation, a colourless solution, which is nearly free from sulphides, and leaves on evaporation a crop of pure salts and a nearly colourless mother-liquor, containing all the iodine and bromine of the seaweed. (For details, see a paper read before the Society of Arts, February 14, 1862; also Pharm. J. Trans. [2] iii. 495; also Richardson and Watts's Chemical Technology, i. [3] 529.)

SEBACIC ACID. $C^{10}H^{18}O^4 = \left.\begin{matrix}C^{10}H^{16}O^2\\H^2\end{matrix}\right\}O^2$. *Pyroleic acid, Sebacylsäure, Fettsäure.* (Thénard, Ann. Chim. xxxix. 193.—Dumas and Péligot, Ann. Ch. Phys. lvii. 332.—Redtenbacher, Ann. Ch. Pharm. xxxv. 188.—Bouis, *ibid.* lxxx. 303; xcvii. 34.—W. Mayer, *ibid.* lxxxiii. 143; xcv. 160.—Rowney, *ibid.* lxxxii. 103.—Carlet, J. Pharm. [3] xxiv. 176.—Arppe, Ann. Ch. Pharm. cxxiv. 98; Jahresb. 1862, p. 283; 1864, p. 377.—Gm. xiv. 494.)—This acid, the highest known term of the oxalic series, $C^nH^{2n-2}O^4$ (i. 52), is produced:—1. By the dry distillation of oleic acid, and of hog's-lard and other fats containing oleic acid or olein (Thénard, Berzelius, Redtenbacher).—2. Together with other acids of the oxalic series, by the oxidising action of nitric acid on fats. Spermaceti thus treated yields sebacic and azelaic acids.—3. Together with heptylic or octylic alcohol, and other products, by distilling castor-oil or ricinoleic acid with excess of caustic alkali. (Bouis and others, 1·98; iii. 144; v. 110.)

Preparation.—Sebacic acid is best prepared from castor-oil by distillation with

fused potash. Delfs (Jahresb. 1862, p. 320) allows 2 pts. of castor-oil to flow into 1 pt. of caustic potash, fused and mixed with a small quantity of water, continuing the heat till the mass assumes a faint yellowish colour. On dissolving the residue in boiling water, and mixing it at the boiling heat with hydrochloric acid, the filtrate, as it cools, yields sebacic acid in bulky needles.

The residue left in the retort in the preparation of heptylic or octylic alcohol from castor-oil, may also be made available for the preparation of sebacic acid. This residue is decomposed by hydrochloric acid, and the sebacic acid is extracted by boiling water from the mixture of insoluble acids thereby separated (Bouis). Petersen (Ann. Ch. Pharm. ciii. 184) boils the residue with water; strains the liquid; precipitates the other fatty acids by adding a small quantity of hydrochloric acid; then, after separating these by filtration, precipitates the sebacic acid by excess of hydrochloric acid, and purifies it by recrystallisation from hot water, with aid of animal charcoal.

The quantity of sebacic acid obtained from fats by dry distillation or by oxidation of nitric acid is very small, and it is difficult to separate the sebacic acid from the other solid acids produced at the same time. According to Arppe, spermacetic and stearic acids yield sebacic acid in larger quantity than other fats.

Properties.—Sebacic acid crystallises in white, nacreous, very light needles or laminæ resembling benzoic acid. It has an acid taste, reddens litmus strongly, does not lose weight at 100°, melts at 127°, solidifies to a crystalline mass on cooling, and sublimes at a higher temperature. The melted acid has a specific gravity of 1·317. Its vapour irritates the palate, and has the odour common to all fatty bodies. It is slightly soluble in cold, very soluble in hot *water*, dissolves very easily also in *alcohol*, *ether*, and *fat oils*.

Decompositions.—1. Sebacic acid heated with strong *nitric acid* dissolves slowly, and is converted into pyrotartaric acid (Schlieper, Ann. Ch. Pharm. lxx. 121); succinic acid (Carlet); succinic, pimelic, and perhaps also adipic acid (Wirz, Ann. Ch. Pharm. civ. 280); succinic and oxypyrolic acids (Arppe, Ann. Ch. Pharm. xcv. 242); according to later experiments, also adipic acid (Jahresb. 1862, p. 377).—2. Sebacic acid is attacked by *pentachloride of phosphorus*, with formation of hydrochloric acid gas, phosphoric oxychloride, and sebacic anhydride (Gerhardt and Chiozza, Compt. rend. xxx. 1050).—3. *Chlorine* acts on sebacic acid only in sunshine, forming two yellow substitution-products, $C^{10}H^{17}ClO^4$ and $C^{10}H^{16}Cl^2O^4$, which are pasty at mean temperature (Carlet).—4. The *calcium-salt* of sebacic acid, subjected to *dry distillation*, gives off hydrogen gas, and yields an oil boiling between 80° and 200°.—On rectifying this oil, a liquid passes over between 85° and 90°, which has a pleasant ethereal odour, and appears to be propionic aldehyde,—then, between 156° and 200°, œnanthol (xii. 446) distils over (Calvi). When sebate of calcium is distilled with *excess of lime*, sebacin (p. 214) is obtained, together with an oil boiling between 80° and 280°. The latter, when rectified, first yields a product which, when treated with nitric acid, forms nitrobenzene, and is therefore probably benzene—then, between 90° and 100°, propionic aldehyde—and at 160° œnanthol, inasmuch as the portions which distil at these temperatures form, with nitric acid, propionic and œnanthylic acids (Petersen, Ann. Ch. Pharm. ciii. 184). By distillation with *excess of baryta*, sebacic acid yields carbonate of barium and a hydrocarbon, $C^{10}H^{18}$, boiling between 125° and 130°, chiefly at 127° (A. Riche, Rép. Chim. pure, ii. 127).—5. When alcoholic sebacic acid is treated with *hydrochloric acid gas*, an oil is produced, which when treated with ammonia forms sebamide and sebacic acid, and is therefore probably a mixture of neutral and acid ethyl-sebacic ether. (Rowney.)

Sebates.—Sebacic acid is dibasic, forming acid and neutral salts. The sebates of the alkali-metals and alkaline earth-metals are soluble in water; the rest are obtained by double decomposition. All the acid sebates, excepting the ammonium-salt, decompose with great facility.

The *neutral ammonium-salt* is very soluble in water, crystallises confusedly, and gives off ammonia in drying. By dry distillation it yields sebamic acid (Kraut).—The *acid salt* forms plumose crystals, slightly soluble in alcohol.—The *potassium-salt*, $C^{10}H^{16}K^2O^8$, crystallises from concentrated solution in small nodules, very soluble in water, non-deliquescent, slightly soluble in absolute alcohol.—The *sodium-salt* is similar, but less soluble in water.—The *calcium-salt*, $C^{10}H^{16}Ca''O^4$ (at 100°) is but slightly soluble in water, and is obtained by precipitation. From a dilute solution it crystallises by spontaneous evaporation, in white, shining, very thin scales.—The *copper-salt* is a greenish-blue precipitate. The mother-liquor, when left to evaporate, yields, on the surface a green crust of crystalline grains. The salt, when heated, melts before decomposing.—The *ferric salt* is a flesh-coloured precipitate, which is decomposed by carbonate of ammonium, part dissolving with red colour, while the rest is changed into an insoluble basic salt. The neutral salt melts when heated, and then decomposes with intumescence.—The *lead-salt* is a white precipitate, converted by ammonia into a basic salt. –

The *mercurous salt* is obtained, as a precipitate, by treating mercurous nitrate either with sebacic acid or an alkaline sebate.—The *silver-salt*, $C^{10}H^{16}Ag^2O^4$, is a white, curdy, nearly insoluble precipitate, obtained with nitrate of silver and an alkaline sebate. When heated in a tube it yields metallic silver and a white crystalline sublimate.

Ipomæic acid. An acid, isomeric with sebacic acid, produced by the action of moderately strong nitric acid on convolvulic acid, convolvulinolic acid, jalapin, jalapic acid, or jalapinolic acid. It resembles sebacic acid in most of its properties and reactions, but melts at a lower temperature, viz. at 104°. The acid and its salts become electric by friction. The precipitate formed by ipomæate of ammonium with chloride of calcium is amorphous at first, and becomes crystalline only after standing for some time, whereas the corresponding precipitate formed by sebate of ammonium, is crystalline when first formed. (W. Mayer, Ann. Ch. Pharm. lxxxiii. 143; xcv. 160.)

SEBACIC ETHERS. *Methylic Sebate*, or *Methyl-sebacic Ether*, $C^{12}H^{22}O^4 = C^{10}H^{16}(CH^3)^2O^4$, is obtained by gradually adding methylic alcohôl to a solution of sebacic acid in strong sulphuric acid, agitating the liquid, and cooling the vessel with cold water. The ether is then precipitated by addition of water, washed first with alkaline, then with pure water, and crystallised from alcohol. It melts at 25·5°, and crystallises in fine needles on cooling. It is heavier than water when solid, but lighter in the melted state. It has a very faint odour; boils without alteration at 285°; is decomposed by potash into potassic sebate and methylic alcohol; and is converted by ammonia into sebamide. (Carlet, Compt. rend. xxxvii. 130.)

Ethylic Sebate, or *Ethyl-sebacic ether*, $C^{14}H^{26}O^4 = C^{10}H^{16}(C^2H^5)^2O^4$, is easily prepared by dissolving sebacic acid in a small quantity of alcohol, and saturating the solution with hydrochloric acid gas. The chloride of ethyl formed at the same time is expelled by a moderate heat; and the product is washed with water containing sodic carbonate, then dried over chloride of calcium, and rectified. It is liquid above —9°, lighter than water, has an agreeable odour, and boils at 308°. It is insoluble in cold water, but dissolves easily in alcohol. Ammonia converts it into sebamide. (Redtenbacher, Ann. Ch. Pharm. xxxv. 193.)

The acid sebates of ethyl and methyl have not been prepared; but they are doubtless formed, together with the neutral ethers, by the action of hydrochloric acid gas on the alcoholic solutions of sebacic acid, inasmuch as these solutions, when treated with ammonia, yield sebamic acid as well as sebamide.

Diglycerylic Sebate or *Sebin*, $C^{16}H^{30}O^8 = \left.\begin{matrix}(C^3H^5)^3\\(C^{10}H^{16}O^2)''\\H^4\end{matrix}\right\}O^6$. — Produced in small quantity as a crystallisable solid, by heating sebacic acid with glycerin to 200°:

$$C^{10}H^{18}O^4 + 2C^3H^8O^3 = C^{16}H^{30}O^8 + 2H^2O;$$

more abundantly, together with chlorhydrin, by the action of hydrochloric acid gas on a mixture of sebacic acid and glycerin heated to 100°. As thus obtained, it is liquid at first, but after drying at 120°, solidifies partially after a few days, and completely at —40°. It gives off acrolein when heated. Oxide of lead converts it into sebacic acid and glycerin. With alcoholic hydrochloric acid, it yields ethylic sebate and glycerin. (Berthelot, Ann. Ch. Phys. [3] xli. 293.)

SEBACIN. $C^{10}H^{18}$.—A hydrocarbon obtained, together with propionic aldehyde, œnanthol, and a small quantity of benzene, by the dry distillation of calcic sebate mixed with excess of lime. It partly condenses, as a solid fatty mass, on the sides of the receiver and the neck of the retort, and partly separates from the liquid product when left at rest. When purified by solution in oil of vitriol, precipitation with water, and recrystallisation from alcohol, it forms nearly colourless laminæ, which easily cake together. It is tasteless and inodorous, lighter than water, melts at 55°, and volatilises at a temperature above 300°. It is insoluble in water, easily soluble in alcohol and ether, dissolves with red colour in oil of vitriol, and is precipitated in its original state by water. It is scarcely altered by nitric acid or caustic potash. (Petersen, Ann. Ch. Pharm. ciii. 187.)

SEBAMIC ACID. $C^{10}H^{19}NO^3 = \left.\begin{matrix}H^2\\(C^{10}H^{16}O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O.\end{matrix}$ (Rowney, Chem. Soc. Qu. J. iv. 334.—Kraut, *Gmelin's Handbook*, xiv. 501.)—Produced: 1. By the action of ammonia on ethyl-sebacic acid (Rowney).—2. By the dry distillation of neutral sebate of ammonium. (Kraut.)

Preparation.—1. The oily mixture of neutral sebacic ether and ethyl-sebacic acid, obtained by the action of hydrochloric acid gas on alcoholic sebacic acid, is digested with strong aqueous ammonia for several weeks in a closed vessel, or till the oil is converted into a granular mass, the sebamide which separates from the liquid containing sebamic acid being removed by filtration, and washed to free it from mother-liquor. The several portions of liquid are then united and concentrated over the water-bath; the sebamic acid is precipitated by hydrochloric acid, washed with cold water, and dissolved in dilute aqueous ammonia, which still leaves a small quantity of sebamide undissolved; the solution filtered therefrom is again precipitated by hydrochloric acid; and the resulting precipitate, after being washed, is purified by recrystallisation from water (Rowney).—2. Neutral sebate of ammonium yields by simple distillation, first a colourless, then a yellowish empyreumatic distillate, which is to be dissolved in ammonia, filtered from a small quantity of oil which separates, and precipitated with hydrochloric acid. The precipitate is washed with cold water, and recrystallised from boiling water. (Kraut.)

Properties.—Sebamic acid forms rounded granules (Rowney); a white, crystalline, pulverulent mass (Kraut). Has an acid reaction (Rowney). It is sparingly soluble in cold, easily in warm water, alcohol, and ammonia. When boiled with calcic carbonate, it gives off carbonic acid, and forms a calcium-salt, slightly soluble in water (Kraut). The solution of sebamic acid in ammonia does not precipitate the alkaline earths; it precipitates *acetate of lead*, and forms, with *nitrate of silver*, a precipitate soluble in ammonia and in nitric acid. (Rowney.)

Sebamic acid gives off ammonia when boiled with *potash* (Rowney).—The sodium-salt brought in contact with *chloride of benzoyl*, yields chloride of sodium and an oil, which may be dissolved out by ether, is left behind when the ether evaporates, gives off ammonia when fused with hydrate of potassium, is insoluble in water and ammonia, and when washed with ammonia, gives up to it only a small quantity of free acid. (Kraut.)

SEBAMIDE. $C^{10}H^{20}N^2O^2 = \left.\begin{matrix}(C^{10}H^{16}O^2)'' \\ H^4\end{matrix}\right\} N^2$. (Rowney, *loc. cit.*—Carlet, Compt. rend. xxxvii. 128.)—Produced as just described from ethylic sebate, or in like manner from methylic sebate, and purified by two recrystallisations from alcohol. It is neutral, and forms hard rounded granules composed of microscopic needles, insoluble in cold, moderately soluble in boiling water; insoluble in ammonia, slightly soluble in cold alcohol, very soluble in boiling alcohol. By water it is gradually converted into sebate of ammonium. It is not attacked by potash in the cold, but gives off ammonia when boiled therewith.

SEBIN. Diglycerylic Sebate. (See SEBACIC ETHERS, p. 214.)

SECALE CEREALE. Rye. See CEREALS (i. 823).

SECALE CORNUTUM. *Ergot.*—These names are applied to several fungi growing on the ears of grasses. They differ in structure and in chemical composition according to the plant on which they grow. Ramdohr (Arch. Pharm. cxxxi. 179) has examined the ergots from rye, from barley, and from *Bromus secalinus*; and finds that they differ in the proportions of organic substance, water, and ash contained in them—also in the composition of the organic substance and of the ash, but the differences are not important. (See *Handw. d. Chem.* vii. 732). Respecting the detection of ergot in rye, see RYE (p. 141).

SECONDARY ALCOHOLS. This term, with its correlatives, primary and tertiary alcohols, has been employed by Kolbe to express certain differences in the manner in which the carbon is linked together in the alcohols. These three terms are borrowed from the nomenclature of the compound ammonias (Ann. Ch Pharm. [1864] lvi. 102). Thus we have:—

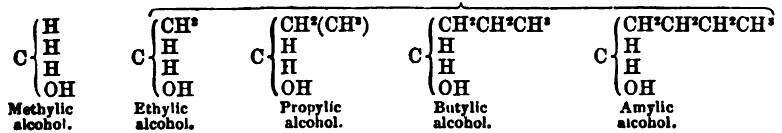
$N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}R\\H\\H\end{matrix}\right.$	$N\left\{\begin{matrix}R\\R\\H\end{matrix}\right.$	$N\left\{\begin{matrix}R\\R\\R\end{matrix}\right.$
Ammonia (type).	Primary amine.	Secondary amine.	Tertiary amine.
$C\left\{\begin{matrix}H\\H\\H\\OH\end{matrix}\right.$	$C\left\{\begin{matrix}R\\H\\H\\OH\end{matrix}\right.$	$C\left\{\begin{matrix}R\\R\\H\\OH\end{matrix}\right.$	$C\left\{\begin{matrix}R\\R\\R\\OH\end{matrix}\right.$
Methylic alcohol (type).	Primary alcohol.	Secondary alcohol.	Tertiary alcohol.

Just as in ammonia there are three atoms of hydrogen capable of replacement by radicles, so in methylic alcohol there are three atoms of hydrogen capable of replacement by radicles. This parallel must not, however, be followed too far, inasmuch as whereas NH^3 takes up HCl (equal to H^2), CH^3 can only take up Cl or OH (equal to H.)

The alcohols obtained by fermentation, the so-called normal alcohols, are believed to be of the primary class. The alcohols obtained by the addition of hydrogen to the ketones are secondary. A tertiary alcohol appears to have been obtained by Buttlerow and by Wanklyn.

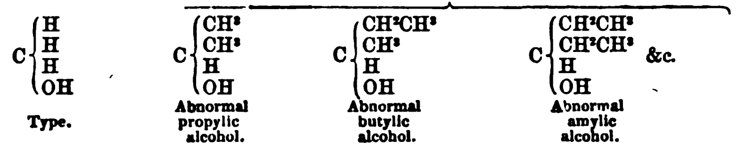
The following formulæ exhibit the structural differences in the three classes of alcohols:—

Primary Alcohols.



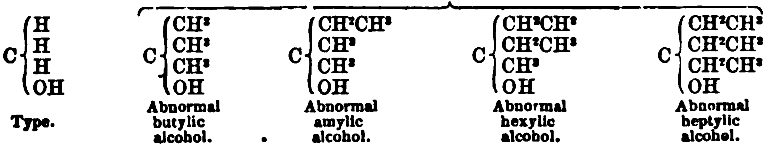
$$C\left\{\begin{matrix}H\\H\\H\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^3\\H\\H\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^2(CH^3)\\H\\H\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^2CH^2CH^3\\H\\H\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^2CH^2CH^2CH^3\\H\\H\\OH\end{matrix}\right.$$

Secondary Alcohols.



$$C\left\{\begin{matrix}H\\H\\H\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^3\\CH^3\\H\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^2CH^3\\CH^3\\H\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^2CH^3\\CH^2CH^3\\H\\OH\end{matrix}\right. \quad \&c.$$

Tertiary Alcohols.


Type.
Abnormal butylic alcohol.
Abnormal amylic alcohol.
Abnormal hexylic alcohol.
Abnormal heptylic alcohol.

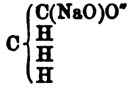
$$C\left\{\begin{matrix}H\\H\\H\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^2CH^3\\CH^3\\CH^3\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^2CH^3\\CH^2CH^3\\CH^3\\OH\end{matrix}\right. \quad C\left\{\begin{matrix}CH^2CH^3\\CH^2CH^3\\CH^2CH^3\\OH\end{matrix}\right.$$

On inspecting these formulæ, it appears that there cannot be a secondary ethylic alcohol, and that neither ethylic nor propylic alcohol is possible in the tertiary series.

The experimental evidence of the existence of these different kinds of structure in different alcohols may be set forth as follows:

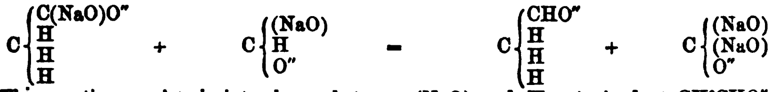
Genesis of the Alcohols of the Primary Type.

Starting with CH^3Na and CO^2 we get—



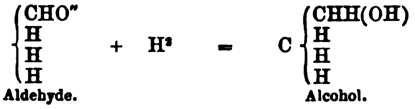
$$C\left\{\begin{matrix}C(NaO)O''\\H\\H\\H\end{matrix}\right.$$

wherein the sodium which saturates one quarter of the one atom of carbon is replaced by an equivalent of the other carbon, whilst the sodium goes to saturate half of one of the atoms of oxygen which existed in combination in the carbonic anhydride. On distilling together $CH^3C(NaO)O''$ and formate of sodium, there is produced aldehyde and carbonate of sodium:



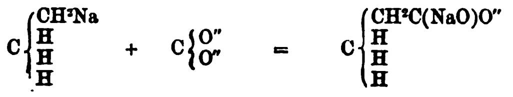
$$C\left\{\begin{matrix}C(NaO)O''\\H\\H\\H\end{matrix}\right. + C\left\{\begin{matrix}(NaO)\\H\\O''\end{matrix}\right. = C\left\{\begin{matrix}CHO''\\H\\H\\H\end{matrix}\right. + C\left\{\begin{matrix}(NaO)\\(NaO)\\O''\end{matrix}\right.$$

This reaction consists in interchange between (NaO) and H. Arrived at CH^3CHO'' (aldehyde), we add nascent hydrogen, and get:



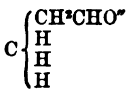
$$\left\{\begin{matrix}CHO''\\H\\H\\H\end{matrix}\right. + H^2 = C\left\{\begin{matrix}CHH(OH)\\H\\H\\H\end{matrix}\right.$$

From alcohol we get iodide of ethyl; from iodide of ethyl we get zinc-ethyl, and then sodium-ethyl, CH^3CH^2Na. Acting upon sodium-ethyl with carbonic anhydride we get:—



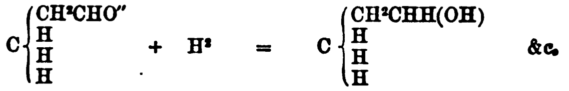
$$C\left\{\begin{matrix}CH^2Na\\H\\H\\H\end{matrix}\right. + C\left\{\begin{matrix}O''\\O''\end{matrix}\right. = C\left\{\begin{matrix}CH^2C(NaO)O''\\H\\H\\H\end{matrix}\right.$$

Whence, as before, by means of formiate:—



$$C\left\{\begin{matrix}CH^2CHO''\\H\\H\\H\end{matrix}\right.$$

Then on addition of hydrogen:—



$$C\left\{\begin{matrix}CH^2CHO''\\H\\H\\H\end{matrix}\right. + H^2 = C\left\{\begin{matrix}CH^2CHH(OH)\\H\\H\\H\end{matrix}\right. \quad \&c.$$

The compound last formulated is the primary propylic alcohol. Now, if the mechanism of these reactions be studied, it will be apparent that the last atom of carbon which is joined on to the group is that which is ultimately combined with the peroxide of hydrogen. We add CO^2, which goes through the stages, $C\overset{''}{O}(ONa)\frac{C}{4}$, $C\overset{''}{O}H\frac{C}{4}$, and $CH(OH)H\frac{C}{4}$.

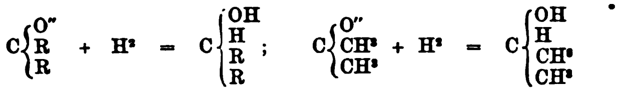
If the formulæ of the primary alcohols be examined, it will appear that one of the chief characteristic structural features of these alcohols is that the atom of carbon which is in combination with the peroxide of hydrogen is in combination with *only one* atom of carbon. This condition is satisfied by the alcohol resulting from the series of reactions above given. It is supposed, but has not been proved, that the alcohols resulting from the fermentation of sugar are identical with those given by the synthetical method.

Genesis of the Alcohols of the Secondary Type.

The formula of a secondary alcohol requires that the same atom of carbon which is in combination with peroxide of hydrogen should be in union with *two* atoms of carbon. This condition is satisfied by forming an alcohol by the addition of hydrogen to a ketone. The constitution of a ketone is this—$C\left\{\begin{matrix}R\\R\\O''\end{matrix}\right.$ as is shown by the general history of the ketones, but most decisively by their formation from carbonic oxide and the compounds of the alkali-metals with the alcohol-radicles:

$$CO + 2NaR = Na^2 + CORR.$$

If then we take a ketone and operate upon its oxygen with nascent hydrogen, the resulting alcohol must contain an atom of carbon which is in direct union with peroxide of hydrogen, and with two atoms of carbon: *e.g.*—

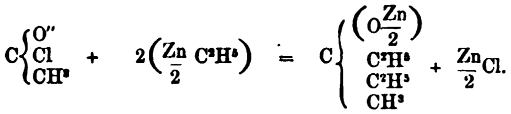


$$C\left\{\begin{matrix}O''\\R\\R\end{matrix}\right. + H^2 = C\left\{\begin{matrix}OH\\H\\R\\R\end{matrix}\right. ; \quad C\left\{\begin{matrix}O''\\CH^3\\CH^3\end{matrix}\right. + H^2 = C\left\{\begin{matrix}OH\\H\\CH^3\\CH^3\end{matrix}\right.$$

The known examples of secondary alcohols are a pseudo- or abnormal propylic alcohol, obtained from acetone and nascent hydrogen, and by attacking glycerin with hydriodic acid, and then decomposing the resulting abnormal iodide of isopropyl with appropriate reagents—a pseudo-butyric alcohol, a pseudo-amylic, and a pseudo-hexylic alcohol, the last-named being obtained from glycerin.

Genesis of the Alcohols of the Tertiary Type.

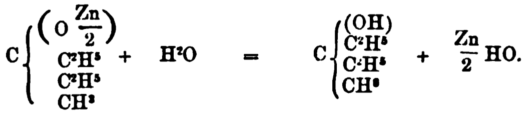
Inspection of the formula of a tertiary alcohol will reveal the fact that a tertiary alcohol must contain an atom of carbon which is in union with *one* atom of peroxide of hydrogen, and *three* of carbon. This structural peculiarity has been realised by Buttlerow, who made chloride of acetyl act on zinc-ethyl as follows:—



$$C\left\{\begin{matrix}O''\\Cl\\CH^3\end{matrix}\right. + 2\left(\frac{Zn}{2}C^2H^5\right) = C\left\{\begin{matrix}\left(O\frac{Zn}{2}\right)\\C^2H^5\\C^2H^5\\CH^3\end{matrix}\right. + \frac{Zn}{2}Cl.$$

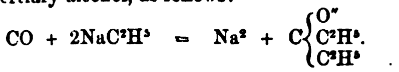
Chloride
of acetyl.

The action of water upon the latter compound gives hydrate of zinc, and the tertiary of alcohol:—

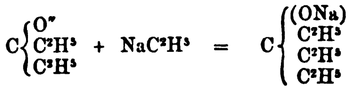


$$C\left\{\begin{matrix}\left(O\frac{Zn}{2}\right)\\ C^2H^5\\ C^2H^5\\ CH^3\end{matrix}\right. + H^2O = C\left\{\begin{matrix}(OH)\\ C^2H^5\\ C^2H^5\\ CH^3\end{matrix}\right. + \frac{Zn}{2}HO.$$

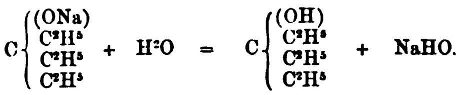
In the reaction between carbonic oxide and sodium-ethyl there appears to result a certain quantity of a tertiary alcohol, as follows:—



$$CO + 2NaC^2H^5 = Na^2 + C\left\{\begin{matrix}O''\\ C^2H^5.\\ C^2H^5\end{matrix}\right.$$



$$C\left\{\begin{matrix}O''\\ C^2H^5\\ C^2H^5\end{matrix}\right. + NaC^2H^5 = C\left\{\begin{matrix}(ONa)\\ C^2H^5\\ C^2H^5\\ C^2H^5\end{matrix}\right.$$



$$C\left\{\begin{matrix}(ONa)\\ C^2H^5\\ C^2H^5\\ C^2H^5\end{matrix}\right. + H^2O = C\left\{\begin{matrix}(OH)\\ C^2H^5\\ C^2H^5\\ C^2H^5\end{matrix}\right. + NaHO.$$

The characters of the tertiary alcohols are almost unknown. The secondary alcohols boil at lower temperatures than the corresponding primary alcohols, and oxidise into ketones instead of into aldehydes. They are apt to evolve their olefine.

J. A. W.

SECONDARY AMIDES and **AMINES.** Compounds derived from a single or multiple molecule of ammonia, by the replacement of two-thirds of the typic hydrogen by acid and basylous radicles respectively (i. 170, 174).

SEIGNETTE SALT. Sodio-potassic tartrate. (See Tartaric Acid.)

SELADONITE. Syn. with Green Earth (ii. 944).

SELBITE. An ash-grey or black silver ore from Wolfach in Baden and the Mexican mines, where it is called *Plata Azul.* It is said to consist mainly of silver-carbonate, but is probably only a mixture.

SELENALDINE. $C^6H^{13}NSe^2$. (Wöhler and Liebig, Ann. Ch. Pharm. lxi. 14.)—A base analogous to thialdine, produced by the action of selenhydric acid on aldehydate of ammonium. To prepare it, the gas is passed into a rather concentrated aqueous solution of the aldehydate, in an apparatus from which the air has been expelled by a current of hydrogen; and when the liquid has deposited crystals of selenaldine, the excess of selenhydric acid gas is likewise expelled by a current of hydrogen. The supernatant liquid containing selenhydrate of ammonium is then displaced by a stream of cold de-aërated water, and the crystals are collected on a filter, pressed, and dried over oil of vitriol.

Selenaldine forms small colourless crystals, probably isomorphous with thialdine, having a faint disagreeable odour, and slightly soluble in water, easily soluble in alcohol and ether, but not crystallisable by evaporation in a vacuum. It is easily decomposed by heat, giving off a fetid gas; when boiled with water it also gives off a very fetid substance, and deposits a yellow powder. Its solution in water, alcohol, or ether yields aldehydate of ammonium on exposure to the air, and deposits an orange-coloured amorphous powder, which is insoluble in alcohol and ether, melts to a yellow-red mass in boiling water, and yields by distillation a very fetid oil containing selenium. Selenaldine dissolves in dilute hydrochloric acid, forming a liquid which is precipitated by ammonia and decomposes quickly, depositing a yellow powder, and emitting an offensive odour.

SELENARSIN. Syn. with Selenide of Cacodyl (i. 408).

SELENETHYL. $(C^2H^5)^2Se$. Already described as Selenide of Ethyl (ii. 544).

SELENHYDRIC ACID. H^2Se. Described as Selenide of Hydrogen (iii. 202). It may also be prepared by heating selenium in a slow stream of pure dry hydrogen gas, forming easily as soon as the selenium assumes the form of vapour. It decomposes at higher temperatures; remains gaseous at —15°. (Uelsmann, Ann. Ch. Pharm. cxvi. 122.)

SELENIC ACID. See Selenium, Oxygen-acids of.

SELENIDES and **SELENHYDRATES.** Selenium unites with metals and with alcohol-radicles, forming compounds analogous in composition, properties, and mode of formation to the sulphides.

Metallic Selenides are obtained in the dry state:—1. By directly fusing the metal with selenium, the combination being often attended with development of light and heat, not so vivid, however, as in the combination of sulphur with the same metals; also by heating the metal in vapour of selenium.—2. By precipitating most of the heavy metallic oxides dissolved in acids, by means of selenhydric acid, or of a disssolved selenide of an alkali-metal, or by heating a hydrated metallic selenide.—3. By heating selenium with metallic oxides or their carbonates, whereby part of the selenium is converted into selenious oxide: thus, the alkalis fused with selenium produce an alkaline selenite and a metallic selenide (Berzelius).—4. By igniting selenites or selenates with hydrogen or charcoal.

The selenides of the alkali-metals have a red or, if they contain excess of selenium, a dark red-brown colour, and the hepatic taste and smell of the corresponding sulphides. Their aqueous solutions, which may be obtained by passing selenhydric acid gas into solutions of the caustic alkalis, are colourless when pure, but are gradually coloured red by free selenium held in solution. On exposure to the air, they decompose, with deposition of crystalline selenium. When selenhydric acid gas is passed to saturation into a solution of caustic alkali, a **selenhydrate** of the alkali-metal, *e.g.* KHSe, is produced.

The selenides of the alkaline earth-metals are flesh-coloured, insoluble in pure water, but soluble in aqueous selenhydric acid; in their other characters they resemble the selenides of the alkali-metals. The selenides of the earth-metals and of manganese and zinc are also flesh-coloured and insoluble in water. The other metallic selenides are mostly dark-coloured, and exhibit the metallic lustre: they are generally more fusible than the metals which they contain. When they are heated to redness in the air, the selenium burns slowly with a reddish-blue flame, and an odour of horseradish. Selenium is, however, more difficult to drive off by roasting than sulphur. The selenides are less easily soluble in nitric acid than the pure metals; selenide of mercury, almost insoluble. Chlorine, with the aid of heat, converts them into chloride of selenium and metallic chloride. Heated in hydrochloric acid gas, they yield metallic chloride and selenhydric acid.

Some metallic selenides occur in nature as rare minerals, or as impurities in sulphides. Selenide of copper occurs as berzelianite at Skrikerum in Sweden, and near Lehrbach in the Hartz; selenide of lead, and selenide of lead and copper, as clausthalite, at Clausthal, Tilkerode, Lehrbach, and other localities in the Hartz; selenide of lead and mercury as lehrbachite at Lehrbach; selenide of silver as naumannite at Tilkerode; selenide of silver and copper, as eucairite, at Skrikerum.

The selenides and selenhydrates (selenium-mercaptans) of the **alcohol-radicles** are volatile fetid liquids resembling the corresponding sulphur-compounds. The ethyl- and methyl-compounds are the only ones yet obtained (ii. 544; iii. 990).

SELENIOCYANATES. $CNMSe = CyMSe$ and $C^2N^2M''Se^2 = Cy^2M''Se^2$.—These compounds, the analogues of the sulphocyanates, were discovered in 1820 by **Berzelius** (Schw. J. xxxi. 60), and have been more fully examined by **Crookes** (Chem. Soc. Qu. J. iv. 12). The potassium-salt is obtained by fusing ferrocyanide of potassium with selenium. The solution of this salt mixed with acetate of lead yields a precipitate of seleniocyanate of lead, which when decomposed by sulphydric acid, yields a solution of hydric seleniocyanate, or seleniocyanic acid; and the other seleniocyanates are obtained by neutralising the acid with bases, or by precipitation, according as they are soluble or insoluble.

Seleniocyanate of Ammonium is a soluble very deliquescent salt, crystallising in minute needles like the potassium-salt.

The *barium-salt* is obtained, but not in definite crystalline form, by dissolving carbonate of barium in the aqueous acid, and evaporating in a vacuum.—The *calcium-salt* crystallises in groups of stellate needles; the *strontium-salt* in fine prisms.

Cupric Seleniocyanate.—Seleniocyanate of potassium added to cupric sulphate throws down a brownish precipitate, which is probably cupric seleniocyanate. It is rapidly decomposed, even at ordinary temperatures, yielding black selenide of copper, with separation of selenhydric acid. (**Crookes**.)

Hydric Seleniocyanate, or *Seleniocyanic Acid*, $CNHSe = CyHSe$, is prepared by passing a rapid stream of sulphydric acid gas through a warm aqueous solution of seleniocyanate of lead in which the same salt is suspended in a state of fine division; heating the filtrate nearly to boiling to expel the excess of sulphydric acid; and again filtering, to separate a small quantity of precipitated selenium. The solution thus obtained is strongly acid, and easily decomposed by boiling or by exposure to the air. It cannot be concentrated without decomposition even in a vacuum over oil of vitriol.

The addition of almost any acid causes an immediate precipitation of selenium, hydrocyanic acid remaining in solution. It dissolves zinc and iron, with evolution of hydrogen, and decomposes carbonates.

Ferric Seleniocyanate.—The rapid decomposition which seleniocyanic acid undergoes in contact with stronger acids, prevents the formation of any red colour with ferric salts by double decomposition. Neither, according to Crookes, is a ferric seleniocyanate obtained by treating ferric oxide with seleniocyanic acid, selenium being immediately precipitated. On one occasion, however, in preparing seleniocyanate of potassium by the process described below, the fused mass having been treated with absolute alcohol in a well-closed flask, a deep blood-red filtrate was obtained, the colour of which soon disappeared on exposure to the air, with deposition of selenium. On other occasions no colour was obtained, the iron always remaining as a black powder, chiefly consisting of carbide of iron.

Seleniocyanate of Lead, $C^2N^2Pb''S^2 = Cy^2Pb''S^2$.—Seleniocyanate of potassium forms, with acetate of lead, a lemon-yellow precipitate, which dissolves, with slight decomposition, in boiling water. The filtered solution, which is neutral to test-paper, deposits, on cooling, beautiful lemon-coloured needles, which are insoluble in alcohol. The salt may be heated to 100° without decomposition, but assumes, when moist, a slight pink tint. The crystals are extremely light. (Crookes.)

Seleniocyanate of Magnesium is soluble, and dries up to a gummy mass apparently destitute of crystalline structure.

Mercuric Seleniocyanate with *Mercuric Chloride*, $C^2N^2Hg''S^2.Hg''Cl^2$.—Obtained by adding an excess of mercuric chloride to seleniocyanate of potassium. When strong solutions are used, the whole immediately solidifies into a felt-like mass of yellowish crystals; these, after washing with water, are purified by recrystallisation from alcohol. The crystals are but sparingly soluble in cold water, but dissolve more readily in hot water, still more in alcohol and in dilute hydrochloric acid; the latter, however, separates selenium after a while. Nitric acid and aqua-regia dissolve the double salt entirely, the liberated selenium being immediately oxidised. The crystals are anhydrous, and may be heated to 100° without decomposition; above that temperature they are decomposed, intumescing in a remarkable manner (Crookes). All attempts to produce the simple seleniocyanate of mercury failed, the double salt just described being always produced

Seleniocyanate of Potassium, $CNKSe = CyKSe$.—Prepared by fusing 1 pt. of selenium with 3 pts. of dry ferrocyanide of potassium in a small retort; digesting the resulting greenish-black mass with absolute alcohol; and passing carbonic anhydride through the solution to decompose cyanide and cyanate of potassium, and precipitate the potassium in the form of acid carbonate (a salt which is quite insoluble in absolute alcohol). The alcohol is then distilled off, together with the hydrocyanic and cyanic acids; and the watery extract of the residue is left to crystallise *in vacuo* over oil of vitriol. The formation of the salt is expressed by the following equation:

$$C^6N^6K^4Fe'' + Se^4 = 4CNKSe + FeC^2 + N^2.$$

The residue in the retort consists chiefly of carbide of iron, together with undecomposed yellow prussiate, and traces of selenium (Crookes). The salt may also be prepared by dissolving selenium in aqueous cyanide of potassium. (Wiggers. Wöhler.)

Seleniocyanate of potassium crystallises in needles, having the same form and taste as the sulphocyanate. It is very deliquescent, and even more soluble than the sulphocyanate. Its solution is decomposed even by weak acids, depositing selenium and giving off hydrocyanic acid. The crystals are strongly alkaline to test-paper, and produce great reduction of temperature when dissolved in water. They may be heated without decomposition in close vessels; but if the air has access to them, they alter when heated a little above 100°.

The *sodium-salt*, obtained by neutralisation, is very soluble, and when evaporated in a vacuum, crystallises in small foliated crystals.

Seleniocyanate of Silver, $CNAgSe$.—The potassium-salt forms with nitrate of silver a curdy precipitate resembling chloride of silver; but if the silver-solution be previously mixed with ammonia, the seleniocyanate of silver is precipitated in beautiful, minute, satiny crystals. This salt blackens readily on exposure to light; is insoluble in water, and very sparingly soluble in cold dilute acids. It is instantly decomposed by boiling with strong acids; and unless oxidising acids are used, selenium is precipitated. (Crookes.)

Seleniocyanate of Zinc, obtained by dissolving either the metal or its oxide in seleniocyanic acid, forms groups of prismatic needles, which are not deliquescent.

SELENIOCYANIC ACID. Syn. with HYDRIC SELENIOCYANATE (p. 219).

SELENIOCYANIC ANHYDRIDE. $C^2N^2Se = \left.\begin{matrix}Cy\\Cy\end{matrix}\right\}Se$.—Produced by the action of iodide of cyanogen on seleniocyanate of silver. It is a volatile crystalline body, closely analogous in all its properties and reactions to sulphocyanic anhydride (*q.v.*). (Linnemann, Ann. Ch. Pharm. cxx. 36.)

SELENIOCYANIC ETHERS. The only one known is the allylic ether, $CN(C^3H^5)Se$, analagous to volatile oil of mustard, which is obtained, though not quite pure, by cohobating 1 at. seleniocyanate of potassium in alcoholic solution with 1 at. allylic iodide for twelve hours, then distilling, and mixing the distillate with water. Allylic seleniocyanate then separates as a heavy yellow oil, which may be obtained colourless by treatment with chloride of calcium and rectification, but does not exhibit a constant boiling-point (150°—184°). The portion boiling at 150° gave by analysis 38·5 per cent. carbon and 42 per cent. selenium, whereas the formula requires 32·6 and 54·4. The compound has an extremely offensive alliaceous odour, and when exposed to the air, gradually turns red from separation of selenium. It differs from the sulphocyanate in not inflaming the skin, and not forming a crystalline compound with ammonia. (Wöhler, Ann. Ch. Pharm. cix. 125).

SELENIOUS ACID. See SELENIUM, OXYGEN-ACIDS OF (p. 226).

SELENITE. Crystallised native sulphate of calcium. (See GYPSUM, ii. 962.)

SELENITES. See SELENIUM, OXYGEN-ACIDS OF (p. 226).

SELENIUM. *Atomic weight*, 79·5. *Symbol*, Se.—An elementary substance belonging to the oxygen-group, and occupying the intermediate place between sulphur and tellurium. It is closely allied in its properties to sulphur, and often associated with that element in the mineral kingdom. It was discovered by Berzelius in 1817, in the refuse of a sulphuric acid manufactory at Gripsholm near Fahlun, in Sweden. Though not an abundant element, it enters into the composition of many minerals. It occurs in the free state at Culebras in Mexico, in crystals, which, according to Mitscherlich, are monoclinic, and in greyish or brownish-black incrustations having a submetallic lustre.* Selenites of cadmium, copper, iron, cobalt, nickel, lead, silver, and mercury, are also found native (p. 219). Selenium frequently occurs as an impurity in native sulphur, as at Vulcano, one of the Lipari Islands, and in metallic sulphides. It occurs to a greater or less extent in the iron pyrites of certain localities, particularly at Fahlun in Sweden, and at Kraslitz and Luckawitz in Bohemia; also in some forms of copper pyrites, those from Rammelsberg and Anglesea, for instance; and occasionally in small quantities associated with the sulphides of lead and molybdenum; also in tellurium-ores, and in pitchblende from Johangeorgenstadt and Schneeberg. The principal sources of selenium are the double selenide of lead and copper found at Clausthal and other places in the Hartz, and the deposit which occurs in the leaden chambers of certain vitriol works, where seleniferous sulphur or pyrites is burned.

Preparation.—1. From the cuproplumbic selenides of the Hartz. The pulverised ore is treated with hydrochloric acid, to dissolve the earthy carbonates, and the washed and dried residue is ignited for some time with an equal quantity of black flux. The selenium is thereby converted into selenide of potassium, which by treatment with boiling water is dissolved away from the oxides formed at the same time. This solution, when exposed to the air, absorbs oxygen, and yields the selenium as a grey deposit, which is washed, dried, and distilled.

2. The seleniferous deposit from certain vitriol works, as those near Fahlun, is mixed with nitrate and carbonate of potassium, and deflagrated in a red-hot crucible. The residue, containing selenate of potassium, is treated with hydrochloric acid, and the whole is evaporated down to a small bulk, whereby a reducing action is set up, and selenious acid is liberated; and on saturating the liquid with sulphurous acid, and heating it to the boiling-point selenium is deposited in red amorphous flakes. For further details respecting both these processes, see *Gmelin's Handbook*, ii. 232.

Another method of obtaining selenium from the deposit of the sulphuric acid chambers, recommended by Liebe (Arch. Pharm. ci. 25), is to treat the deposit with nitromuriatic acid; expel the excess of this acid by heat, after addition of sulphuric acid; wash the residue when cold with water; neutralise the solution with sodic carbonate; evaporate to dryness; roast the residue at a gentle heat with an equal weight of sal-ammoniac, till it becomes red-brown (nitrogen and sal-ammoniac being then given off, but no appreciable quantity of selenium); and treat the red-brown mass with water, which leaves the selenium undissolved.

3. Böttger has shown that the flue-dust of the roasting furnaces in the desilverising works at Mansfeld, in Saxony, contains uncombined selenium in quantity sufficient for profitable extraction (9 per cent. according to Kemper, Arch. Pharm. [2] ci. 25).

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* This native selenium is sometimes called *Riolite*, from Del Rio, who discovered it; but that name is also applied to selenide of silver, found by the same mineralogist at Tasco in Mexico (p. 111).

To separate the selenium, Böttger levigates the flue-deposit; washes out the heavier parts with water containing hydrochloric acid, and with pure water; then fuses it with crude sodic or potassic carbonate; pulverises the fused mass, lixiviates it, and leaves the brown-red liquid exposed to the air; then separates the deposited selenium by filtration, and distils it. (J. pr. Chem. lxxi. 512.)

Properties.—Selenium, like sulphur, occurs in different allotropic states, both amorphous and crystalline. These modifications have been especially studied by Hittorf (Pogg. Ann. lxxxiv. 214; Jahresb. 1851, p. 318), Mitscherlich (J. pr. Chem. lxvi. 301; Jahresb. 1855, p. 314), and Regnault (Ann. Ch. Phys. [3] xlvi. 257; Jahresb. 1856, p. 44.)

1. *Amorphous.*—Selenium, precipitated from a solution of selenhydric acid by exposure to the air, or by electrolysis (electronegative selenium), is amorphous, and soluble in sulphide of carbon; that which is deposited from aqueous selenious acid, either by electrolysis or by the reducing action of sulphurous acid (electropositive selenium), is likewise amorphous, but insoluble in sulphide of carbon.

Amorphous selenium softens when heated, becomes semifluid at 100°, and perfectly fluid at a somewhat higher temperature (Berzelius, *Traité de Chimie* [1846], ii. 190). On cooling, the selenium remains soft for a long time, and may be drawn out, like sealing-wax, into long thin flexible threads, which when flattened are transparent, and of a deep ruby colour by transmitted light. When quickly cooled from fusion, it forms a brittle solid, having a glassy fracture, almost metallic lustre, and deep brown colour. This *vitreous* selenium has a specific gravity of 4·3, is nearly insoluble in sulphide of carbon, does not conduct electricity, but becomes slightly electrical by friction in a dry atmosphere.

2. *Crystalline.*—*a.* Selenium, when very slowly cooled from the fused state, forms a lead-grey mass having an irregular granular surface and fine-grained fracture (Berzelius). Vitreous selenium remains unaltered at ordinary temperatures, but at temperatures between 80° and 217°, most quickly between 125° and 180°, it becomes crystalline, the change being attended with considerable rise of temperature (Hittorf). According to Regnault, vitreous selenium remains unaltered, even when heated to 90° for several hours; but at 96° or 97° it passes quickly, and with great evolution of heat, into the crystalline state, acquiring a bluish-grey colour, metallic lustre, and granular fracture. According to Mitscherlich, the change from the vitreous to the crystalline state is most easily effected by melting the selenium in a flask, heating it above 217°, then quickly cooling it to 180°—190°, and keeping it for some time at this temperature. This crystallo-granular selenium is quite insoluble in sulphide of carbon. According to Hittorf, it melts at 217° without previous softening; but according to Regnault, it gradually softens when heated, and does not become completely fluid till heated above 250°.

β. Selenium deposited from a solution of selenide of ammonium, potassium, or sodium, on exposure to the air, is likewise crystalline, and has a specific gravity of 4·808 at 15° (Hittorf); 4·760—4·788 at 15° (Mitscherlich). It is likewise insoluble in sulphide of carbon, and, according to Mitscherlich, is identical in every respect with the crystallo-granular variety obtained by the transformation of vitreous selenium. Crystalline selenium conducts electricity better than the vitreous modification, and the more easily as its temperature is higher.

γ. Selenium is deposited from solution in sulphide of carbon in small but distinct crystals, which, according to Mitscherlich, are monoclinic, exhibiting the dominant faces, oP, 0+P, −P, together with numerous secondary faces. Axes $a : b : c = 0·6170 : 1 : ·9622$. Angle $b : c = 75° 34'$; oP : +P = 112° 36′; oP : −P = 124° 48′ : ∞P∞ : +P = 111° 48′; ∞P∞ : − P = 123° 63′. These crystals dissolve easily, though sparingly, in sulphide of carbon, 100 pts. of that liquid dissolving 1 pt. of selenium at the boiling heat, and 0·016 pt. at 0°. They retain their solubility after being heated to 100°, but if heated to 150°, becomes nearly black and quite insoluble in sulphide of carbon; the selenium thus modified regains its solubility by melting and rapid cooling. The crystals before being heated have a specific gravity of 4·46 to 4·509 at 15°; after heating, it increases to 4·7°, being then nearly equal to that of the variety deposited from solutions of alkaline selenides. Crystalline selenium appears indeed to be dimorphous, the two varieties being probably related to one another in the same manner in monoclinic and rhombic sulphur (ii. 332). Native selenium (p. 221) appears to be monoclinic (Mitscherlich); its specific gravity is 4·3—4·2, and hardness 2·0.

Amorphous and crystalline selenium exhibit, according to Regnault, a considerable difference of specific heat at comparatively high temperatures. He found the specific heat of crystalline selenium between 98° and 20° to be = 0·0762; that of amorphous selenium considerably greater—viz., 0·1036 between 87° and 19°, and 0·1026 between 77° and 18°. At lower temperatures, however, as between −20° and 7°, the specific heats of the two modifications are sensibly equal. The change from the amorphous to the crystalline state is attended with the evolution of a quantity of heat sufficient, according to Regnault, to raise the temperature of the selenium 200 degrees. Mitscherlich, however, found the rise of temperature to be much smaller, viz. 20°; and according to Hittorf, it is only 5° (the thermometer rising from 210° to 215°).

Selenium heated in close vessels boils below a red heat, and is converted into a deep yellow vapour, which condenses in scarlet flowers or black lustrous drops, according to the size of the condenser. At temperatures not much above its boiling-point, the density of its vapour, like that of sulphur under similar circumstances, is anomalous; but at higher temperatures it diminishes, and ultimately the vapour occupies a bulk nearly equal to that of an equivalent quantity of oxygen. According to Deville and Troost (Ann. Ch. Pharm. cxxvii. 274), the vapour-density of selenium is 7·67 at 860°, 6·37 at 1040°, and 5·68 at 1420°, the calculated density for a two-volume condensation being 5·54.

Selenium is quite insoluble in water, whether cold or hot. It dissolves to a slight amount in oil of vitriol, but is precipitated on dilution. Its relations to sulphide of carbon have already been mentioned. Monoclinic selenium and the amorphous variety deposited from selenhydric acid are soluble in that liquid; the vitreous modification is very slightly soluble; and the crystallo-granular variety, the crystalline selenium deposited from alkaline selenides, and the amorphous variety deposited from selenious acid, are quite insoluble.

Selenium does not take fire very readily, but when thoroughly heated in contact with air, it burns with a blue flame, forming selenious anhydride, giving off yellowish-red vapours of unoxidised selenium, and emitting an odour like that of decayed horseradish, probably due to a protoxide of selenium formed at the same time. When heated in a current of oxygen gas, it is wholly converted into selenious anhydride. It unites directly with bromine and chlorine, and, when heated, also with iodine, sulphur, phosphorus, and metals. It is oxidised and dissolved by nitric and nitromuriatic acid, yielding selenious acid.

SELENIUM, BROMIDE OF. When pulverised selenium is dropped by small quantities into bromine, combination takes place, attended with loud hissing and considerable evolution of heat; and the compound instantly solidifies to a brown-red or orange-red mass, which fumes in the air and smells like chloride of sulphur. It volatilises when heated, part being resolved into selenium and bromine, while the rest sublimes as a yellow mass. Water dissolves and decomposes it, forming hydrobromic and selenious acids. (Serullas.)

SELENIUM, CHLORIDES OF. There are two chlorides of selenium, both formed by direct combination. The *dichloride*, Se^2Cl^2, or *perselenide of chlorine*, analogous to persulphide of chlorine, S^2Cl^2, and persulphide of hydrogen, H^2S^2, was discovered by Berzelius, who obtained it by heating the tetrachloride with selenium. According to Sacc (Ann. Ch. Phys. [3] xxiii. 124), it may be obtained by passing a slow stream of dry chlorine through an inclined glass tube filled with fragments of fused selenium. The heat evolved by the reaction volatilises the chloride of selenium, which condenses in the colder parts of the tube, and flows in thick drops through the open end into a perfectly dry receiver.

Dichloride of selenium is a dark-yellow oily liquid, having a pungent odour, not very volatile according to Berzelius, extremely volatile according to Sacc. It is slowly decomposed by cold, quickly by hot water, into hydrochloric acid, selenious acid, and free selenium; but the decomposition is seldom complete, because a portion of the dichloride generally becomes mechanically enclosed in the solid selenium.

Tetrachloride of Selenium, $SeCl^4$, is produced by passing chlorine gas over fused selenium, contained in a bulb-tube. The liquid dichloride is at first produced, and is afterwards converted into a white solid mass of the tetrachloride, which when further heated, volatilises as a yellow vapour, and sublimes on the colder parts of the apparatus in small thin crystals. By prolonged heating, the crystals aggregate into a white semi-fused mass, which becomes fissured on cooling. Tetrachloride of selenium dissolves in water with rise of temperature and slight effervescence, forming a solution of hydrochloric and selenious acids: $SeCl^4 + 3H^2O = 4HCl + H^2SeO^3$ (Berzelius, Ann. Ch. Phys. [2] ix. 225). When decomposed by a small quantity of water, or by exposure to moist air, it yields oxychloride of selenium, $SeCl^2O$ or $SeCl^4.SeO^2$ (p. 224).

When a selenate is heated with common salt and sulphuric acid, tetrachloride of selenium mixed with free chlorine passes over first, and then green vapours, which condense to an oily mixture of selenious and sulphuric acids. (H. Rose, Pogg. Ann. xxvii. 575.)

Tetrachloride of selenium gradually absorbs vapour of sulphuric anhydride, especially when the two substances are enclosed in a closely-corked vessel and placed in a warm room; they then unite, without disengagement either of sulphurous anhydride or of chlorine, and form a very dense greenish-yellow syrup, the excess of sulphuric anhydride remaining in the crystalline form. On distilling the syrup at a gentle heat, the excess of sulphuric anhydride passes over first, and the residue in the retort solidifies on cooling to a white crystalline mass. This, when more strongly heated, melts to a light-brown liquid, and evolves (with disengagement of chlorine, but not of sulphurous anhydride) a reddish-yellow vapour resembling nitric peroxide, which condenses to a colourless syrup, and finally to a white mass resembling wax. The latter substance is freed from adhering chlorine by a second distillation. After this treatment, it boils constantly at 187°, and may be redistilled without leaving any residue or undergoing further decomposition. It contains, on the average, 12·895 per cent. of selenium and 36·885 of chlorine; and, according to H. Rose, may be regarded as $2(SeCl^6.5SO^3) + 5(SeCl^4.SeO^2)$. Berzelius, on the other hand, regards it as consisting mainly of the compound $SeCl^4.SO^3$, analogous to the compounds of sulphuric anhydride with other chlorides. It deliquesces rapidly in the air, exhaling the odour of hydrochloric acid; and dissolves readily in water, without first sinking to the bottom in oily drops; the solution, which is generally coloured red, from the presence of a small quantity of free selenium, contains hydrochloric, sulphuric, and selenious acids (no selenic acid). (H. Rose, Pogg. Ann. xliv. 315.)

SELENIUM, CYANIDES OF. Syn. with SELENIOCYANIC ANHYDRIDE (p. 220).

SELENIUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe-reactions.*—Metallic selenides heated in the outer flame, and selenites or selenates heated in the inner flame, on charcoal, give off a characteristic odour, like that of decayed horseradish. When a metallic selenide is heated in the outer flame on charcoal, the charcoal generally becomes covered, at some distance from the bead, with a steel-grey, slightly metallic deposit of selenium, which may be easily driven by the oxidising flame from one part to another. Selenium-compounds heated on charcoal with carbonate of sodium yield a residue of selenide of sodium, which when placed on a clean silver surface and moistened with a drop of water, produces a black stain. When a metallic selenide is heated in an inclined glass tube open at both ends, part of the selenium is volatilised in the free state, and forms a red sublimate on the upper part of the tube, the metal being at the same time oxidised. Sometimes also selenious oxide is formed, and deposited on the colder part of the tube in a network of crystals.

2. *Reactions in Solution.*—Selenhydric acid and solutions of alkaline selenides deposit selenium on exposure to the air, the former yielding it in red amorphous flakes, the latter as a grey crystalline film (p. 222). Selenides heated with *acids*, give off selenhydric acid gas, which is inflammable, has a peculiar fetid odour, and forms dark-coloured precipitates with most metallic solutions (iii. 202).

Soluble selenites give with *sulphurous acid* and other reducing agents, a red precipitate of free selenium, and with *sulphydric acid*, a lemon-yellow precipitate of sulphide of selenium. Soluble selenates give with *chloride of barium*, a precipitate of barytic selenate, which is insoluble in cold dilute acids; but when heated with hydrochloric acid, gives off chlorine and is reduced to selenite of barium, which dissolves.

3. *Estimation and Separation.*—The methods adopted for the quantitative estimation of selenium vary according to the nature of the compound to be analysed. When the selenium is contained in a solution in the form of selenious acid or a selenite, the solution is acidulated with hydrochloric acid, and mixed with an *alkaline sulphite*. The selenium is thereby reduced and precipitated as a red powder, which, on heating the liquid, cakes together and turns black. The treatment with alkaline sulphite must be repeated till no more red coloration is produced. The precipitate is then to be collected on a weighed filter, washed, dried at a gentle heat, and weighed. If the solution likewise contains nitric acid, this acid must be decomposed by boiling with hydrochloric acid before adding the alkaline sulphite.

When selenium is present in solution as selenic acid, the liquid must be boiled with *hydrochloric acid* to convert the selenic into selenious acid, from which the selenium may then be precipitated by an alkaline sulphite as above. The precipitation of selenic acid as a barium-salt does not give very exact results, because selenate of barium is not quite insoluble in dilute acids, and, moreover, has even a greater tendency than the sulphate to carry down other salts, which cannot be separated from it by washing with hot water. Insoluble selenates, like selenate of barium, which are but slowly reduced to selenites by boiling with hydrochloric acid, must first be decomposed by digestion with a solution of alkaline carbonate. If, however, the selenate of barium be mixed with sulphate, the decomposition of the former by aqueous alkaline carbonates is never complete; hence sulphate and selenate of barium cannot be separated by this method (H. Rose, Pogg. Ann. cxiii. 472, 621; Jahresb. 1861, p. 828). The quantities of these two salts in a mixture may, however, be ascertained by an indirect method.

A weighed quantity of the mixed barium-salts is fused with a mixture of potassic and sodic carbonates in equivalent proportions; the soluble salts are washed out; and the residual barium-carbonate is weighed. If now the weight of barium-sulphate equivalent to this weight of carbonate be subtracted from the weight of the mixture of sulphate and selenate, and the difference be multiplied by $\frac{140{\cdot}5}{140{\cdot}5 - 116{\cdot}5} = \frac{140{\cdot}5}{24}$ (since $BaSO^4 = 140{\cdot}5$ and $BaSO^4 = 116{\cdot}5$), the product will give the quantity of barium-selenate in the mixture. (Wohlwill, *Handw. d. Chem.* vii. 800.)

Selenites and selenates may also be analysed by fusing them with 7 or 8 pts. of *potassium-cyanide* in an atmosphere of hydrogen. The whole of the selenium is thereby converted into seleniocyanate of potassium, the aqueous solution of which when boiled for some sime (to convert any selenide of potassium that may be present into seleniocyanate), and supersaturated when cold with hydrochloric acid, deposits the whole of the selenium in the course of 12 to 24 hours. The selenium may then be dried at 100° and weighed. Free selenious or selenic acid in solution may be neutralised with an alkaline carbonate, the solution evaporated to dryness, and the residue treated as just described. (Oppenheim, J. pr. Chem. lxx. 266; H. Rose, *loc. cit.*)

Selenium may also be separated from sulphur and tellurium by fusing the mixture, in which the selenium and tellurium may both exist as oxygen-acids, with 10 pts. of cyanide of potassium in a long-necked flask through which a stream of hydrogen is passed. The selenium and sulphur are thereby converted into seleniocyanate and sulphocyanate, and the tellurium into telluride of potassium; and on passing a stream of air through the aqueous solution of the product, the whole, of the tellurium is precipitated in the free state, and the filtrate, treated with hydrochloric acid as above, deposits the selenium, while the sulphur remains in solution. From a finely-pulverised mixture of sulphur and selenium, the whole of the selenium may be dissolved out by digestion with a warm solution of potassium-cyanide, which also takes up part of the sulphur. The undissolved sulphur is then collected and weighed, the selenium precipitated from the filtrate by hydrochloric acid, the dissolved sulphur oxidised by chlorine to sulphuric acid, and precipitated by a barium-salt (H. Rose). Small quantities of selenium may be detected in sulphur by boiling with aqueous potassium-cyanide, the solution, if selenium is present, exhibiting a reddish turbidity when treated with hydrochloric acid.

Metallic Selenides are best analysed by heating them in a stream of *chlorine*, the selenium then volatilising as di- and tetrachloride, while the metallic chloride in most cases remains behind. The chlorides of selenium are collected in water, whereby a solution of selenious and selenic acids is formed. This is heated with hydrochloric acid, to reduce the selenic to selenious acid, and the selenium is precipitated therefrom by an alkaline sulphite as above. In applying this method to the selenides of lead and zinc, care must be taken not to apply too strong a heat, as the chlorides of these metals are somewhat volatile. The chlorides of mercury, arsenic, and antimony pass over into the receiver, and are dissolved together with the chlorides of selenium. The presence of arsenic or antimony does not interfere with the precipitation of the selenium by sulphurous acid; but mercury would be precipitated at the same time, in the form of calomel. In this case, therefore, the whole of the selenious acid must be converted into selenic acid by saturating the liquid with chlorine; the selenic acid precipitated by a barium-salt, the excess of barium removed by sulphuric acid, and the mercury precipitated as calomel by an alkaline formate.

4. *Atomic Weight of Selenium.*—Numerous attempts have been made to determine the atomic weight of selenium by the analysis of selenites and selenates, but the results are by no means accordant (*Handw. d. Chem.* 2^{te} Auflage, ii. [2] 500). Berzelius found that 100 parts of selenium heated in a current of chlorine yielded 279 pts. of tetrachloride, $SeCl^4$: whence $Se = \frac{4Cl \times 100}{179} = 79{\cdot}32$. Dumas (Ann Ch. Pharm. cxiii. 31), by a similar method, taking care to condense the chloride of selenium completely by passing the excess of chlorine through a tube cooled to −20°, and then through another filled with asbestos, obtained, as a mean of seven experiments, $Se = 79{\cdot}46$.

SELENIUM, FLUORIDE OF. Obtained, according to Knox, by heating fluoride of lead in selenium-vapour, selenide of lead then remaining, while the fluoride of selenium sublimes in crystals. It volatilises undecomposed at higher temperatures, dissolves in strong hydrofluoric acid, but is immediately decomposed by water into hydrofluoric and selenious acids.

SELENIUM, IODIDES OF. Not known with certainty. Equivalent quantities of iodine and selenium melt together when heated, to a blackish-grey mass, from which the whole of the iodine is extracted by absolute alcohol. (Trommsdorff.)

SELENIUM, OXIDES AND OXYGEN-ACIDS OF. The only oxide of selenium whose composition is exactly known is the dioxide or selenious anhydride, SeO^2, the hydrate of which is selenious acid, H^2SeO^3. A lower oxide is produced by the imperfect combustion of selenium in air or oxygen, but its composition has not been ascertained. It is a colourless gas, which is the source of the peculiar horseradish odour evolved in the combustion of selenium; it is sparingly soluble in water, but has no acid reaction. The trioxide, or anhydride of selenic acid, $H^2O.SeO^3$, has not been isolated.

Dioxide of Selenium, Selenious Oxide or **Anhydride,** SeO^2.—This compound, the analogue of sulphurous oxide, SO^2, is produced by burning selenium in a stream of oxygen; or by evaporating the solution of selenious acid to dryness. In the latter case it is obtained as a white mass which does not melt, but, at a heat somewhat below redness, volatilises in the form of a yellow vapour, which condenses in white four-sided needles. It absorbs water rapidly, producing selenious acid.

Selenious Acid, $H^2SeO^3 = \left.\begin{matrix}(SeO)''\\H^2\end{matrix}\right\}O^2$.—This acid is produced by the hydration of selenious oxide, or by the action of nitric or nitromuriatic acid on selenium. From its hot aqueous solution, it is deposited, on slow cooling, in prismatic crystals like those of saltpetre, which readily absorb water, but effloresce in dry air. When heated it splits up into water and the anhydride, which sublimes at a higher temperature. Its solution has an acid taste, and is reduced, especially at the boiling heat, by *sulphurous acid* or a *sulphite*, with deposition of red amorphous selenium; also by *stannous chloride*, and by all *metals*, except gold, palladium, and platinum, but not by ferrous sulphate. *Sulphydric acid* throws down from its solution a yellow precipitate, usually regarded as disulphide of selenium, but consisting, according to H. Rose (Pogg. Ann. cvii. 186), merely of a mixture of selenium and sulphur:

$$H^2SeO^3 + 2H^2S = 3H^2O + Se + S^2$$

Selenious acid is not decomposed by boiling with hydrochloric acid. It is oxidised to selenic acid by *chlorine* in presence of water, by *potassic chromate*, *peroxide of manganese*, and *peroxide of lead*, and by fusion with *saltpetre*.

Selenious acid is a very powerful acid, approximating to sulphuric acid in the energy of its reactions. It reddens litmus, neutralises alkalis completely, effervesces with carbonates, and being non-volatile, decomposes chlorides and nitrates with aid of heat. Its aqueous solution precipitates the neutral salts of lead and silver.

Selenites.

Selenious acid is dibasic, forming neutral salts, M^2SeO^3 and $M''SeO^3$, and acid salts, $HMSeO^3$ and $H^2M''Se^2O^6$. The acid selenites of the alkali-metals also form double or hyperacid salts, with an additional quantity of selenious acid: *e.g.* $HKSeO^3.H^2SeO^3$. The neutral selenites have a purely saline taste. They are decomposed by heating with *charcoal*, yielding selenides, or metallic oxide and selenium. When heated with *carbonate of sodium* in the inner blowpipe-flame, they emit the characteristic horseradish odour. The fused mass moistened with water produces a brown stain on silver. Heated with *chloride of ammonium*, out of contact with the air, they yield a sublimate of metallic selenium. The selenites of the alkali-metals are soluble in water, and their solutions, acidulated with hydrochloric acid, behave like the free acid with sulphurous acid, sulphydric acid, &c. The other selenites are insoluble in water, but soluble in nitric acid; the lead- and silver-salts, however, dissolve but slowly. The selenites have been examined chiefly by Berzelius and by Muspratt. (Chem. Soc. Qu. J. ii. 52.)

SELENITES OF ALUMINIUM.—The *neutral salt*, $Al^2O^3.3SeO^2 = \left.\begin{matrix}(Se''O)^3\\(Al''')^2\end{matrix}\right\}O^6$, obtained by precipitating an aluminium-salt with neutral selenite of potassium, is a white powder insoluble in water, and decomposing when strongly heated, giving off first water and then the whole of its acid (Berzelius).—An *acid salt* is formed by dissolving the neutral salt or aluminium-hydrate in selenious acid, and is obtained by evaporation as a colourless, gummy, transparent mass, having a harsh taste and easily soluble in water. (Berzelius.)

SELENITES OF AMMONIUM.—The *neutral salt*, $(NH^4)^2SeO^3$, is obtained in shining deliquescent crystals, by saturating alcoholic selenious acid with ammonia-gas (Muspratt); also by leaving a solution of the acid in excess of aqueous ammonia to evaporate in a warm place. When heated it gives off water and ammonia, and afterwards water and nitrogen, together with a small quantity of the hyperacid salt, and leaves a residue of fused selenium:

$$3(NH^4)^2SeO^3 \quad = \quad 9H^2O \; + \; 2NH^3 \; + \; 2N^2 \; + \; Se^3.$$

The *acid salt*, produced, with evolution of ammonia, by leaving an aqueous solution of the neutral salt to evaporate, forms needles permanent in the air (Berzelius).—The *hyperacid salt*, obtained by evaporating a solution of the preceding, with aid of heat, or with addition of selenious acid, is deliquescent and uncrystallisable. (Berzelius.)

Selenites of Barium.—The *neutral salt*, $Ba''SeO^3$, separates from a mixture of barium-chloride and neutral potassium-selenite, as a white precipitate, insoluble in water, easily soluble in acids. It does not fuse even at the melting-point of glass (Berzelius). According to Muspratt, it separates from a mixture of barium-nitrate and potassium-selenite, in delicate, shining, feathery crystals.—The *acid salt* is obtained by dissolving barium-carbonate in selenious acid, and leaving the solution to evaporate, in crystalline granules, sparingly soluble in water. Ammonia added to the solution throws down the neutral salt (Berzelius). When strongly heated it gives off white fumes of selenious oxide. (Muspratt.)

Selenite of Cadmium, $Cd''SeO^3$, is a white precipitate, which becomes orange-yellow on exposure to the air, and yields a yellowish sublimate when heated in a glass tube. It is anhydrous, and soluble in selenious acid. (Muspratt.)

Selenites of Calcium.—The *neutral salt*, $Ca''SeO^3$, separates as a soft crystalline powder from a solution of calcium-carbonate in selenious acid. It is sparingly soluble in water, and melts at a bright red heat (Berzelius).—An *acid salt* crystallises from a solution of the neutral salt in excess of selenious acid, in very small prisms, which are permanent in the air at ordinary temperatures, but give off half their acid when heated, or in contact with ammonia. (Berzelius.)

Selenites of Cerium.—The *neutral cerous salt* is a white powder, insoluble in water, soluble in selenious acid.—The *neutral ceric salt* is a lemon-yellow powder, which when heated gives off its acid and leaves ceric [? ceroso-ceric] oxide. It dissolves in selenious acid, forming an *acid salt*, which dries up on evaporation to a yellow varnish, and when heated gives off water, becoming opaque and crystalline. (Berzelius.)

Chromic Selenite, $Cr^2O^3.3SeO^2 = \left.\begin{matrix}(Se''O)^3\\(Cr''')^2\end{matrix}\right\}O^6$, is obtained by precipitating chromic chloride with selenite of ammonium, as a green amorphous powder, the solution of which in selenious acid leaves a green varnish on evaporation. (Muspratt.)

Selenite of Cobalt.—The *neutral salt*, $Co''SeO^3$, is a pale-red powder, insoluble in water.—The *acid salt* is soluble, and remains on evaporation as a purple-red varnish. (Berzelius.)

Selenites of Copper.—The *neutral cupric salt*, $Cu''SeO^3$, is precipitated on adding the acid ammonium-salt to a warm solution of cupric sulphate, in bulky, curdy, yellowish flocks, quickly converted by heat into small, silky, greenish-blue crystals, which at a higher temperature give off water and turn liver-brown, then melt, and ultimately give off all their acid. The salt is insoluble in water and in selenious acid (Berzelius). According to Muspratt, it turns blue over oil of vitriol, and has the composition $3Cu''SeO^3.H^2O$.—A *basic cupric selenite* is precipitated on mixing cupric sulphate with ammonium-selenite containing excess of ammonia, as a pistachio-brown powder, insoluble in water but soluble in ammonia. When heated it first loses water, then froths up, and gives off all its acid. (Berzelius.)

Cuprous Selenite is a white insoluble powder, obtained by digesting cuprous hydrate with selenious acid. (Berzelius.)

Selenites of Glucinum.—The *neutral salt* is a white insoluble powder, which leaves glucina when ignited. The acid salt is gummy and soluble in water. (Berzelius.)

Selenites of Iron.—The *neutral ferric salt*, $Fe^2O^3.3SeO^2 = \left.\begin{matrix}(Se''O)^3\\(Fe''')^2\end{matrix}\right\}O^6$, obtained by double decomposition, is a white insoluble powder, which becomes somewhat yellowish on drying, gives off water at a higher temperature, then turns red, and gives off all its acid (Berzelius).—An *acid ferric selenite* crystallises on cooling from a solution of iron in an excess of mixed selenious and nitric acids, in pistachio-green laminæ. When heated it gives off water, gradually blackens and gives off its acid, and ultimately leaves a residue of ferric oxide. It is insoluble in water, but dissolves with orange-yellow colour in hydrochloric acid (Berzelius).—A *basic ferric selenite*, insoluble in water, is obtained by treating either of the preceding salts with ammonia. (Berzelius.)

Neutral ferrous Selenite, $Fe''SeO^3$, is a white precipitate, gradually turning grey, and ultimately yellow, on exposure to the air. Its solution in selenious acid yields an *acid salt*, $Fe''SeO^3.SeO^2$, slightly soluble in water; the solution, when heated, yields a brown precipitate, consisting of selenium and ferric selenite. (Berzelius.)

Selenites of Lead.—The *neutral salt*, $Pb''SeO^3$, obtained by precipitating aqueous chloride of lead with excess of ammonium-selenite, is a white heavy powder, nearly insoluble in water, slightly soluble in nitric acid, and melting, almost as easily as chloride of lead, to a yellowish transparent liquid, which solidifies to a white opaque mass having a crystalline fracture. By exposure to a strong red heat, or by treatment with ammonia, it is converted into a *basic salt*, which forms a translucent, friable, fusible mass, also having a crystalline fracture.—According to Kersten (Pogg. Ann. xlvi. 277), neutral selenite of lead occurs native; but, according to H. Rose, the mineral thus characterised is a selenate (p. 232).

Selenites of Magnesium.—The *neutral salt*, $Mg''SeO^3.3H^2O$ (Muspratt), remains, on treating carbonate of magnesium with selenious acid, as a granular powder, insoluble in cold, slightly soluble in hot water, and separating therefrom, on evaporation and cooling, in small four-sided prisms or tables. At a higher temperature it gives off its water, and acquires a fused appearance, but without actually melting or giving off acid, and attacks the glass strongly (Berzelius).—The *acid salt* is precipitated by alcohol from a solution of the neutral salt in selenious acid, as a crystallisable, pasty, deliquescent mass. (Berzelius.)

Selenites of Manganese.—The *neutral salt* is, according to Berzelius, a soft, white, easily fusible powder, which melts and decomposes when heated, and, in the fused state, attacks glass strongly. It is insoluble in water. Muspratt, by dissolving carbonate of manganese in selenious acid, obtained a white sandy powder having the composition $Mn''SeO^3.2H^2O$, which formed a colourless solution with cold, and a pale-red solution with hydrochloric acid.—The *acid salt* is crystallisable, very soluble in water, and gives off half its acid when heated out of contact with the air.

Selenites of Mercury.—The *neutral mercuric salt*, $Hg''SeO^3$, obtained by double decomposition, or by bringing mercuric oxide in contact with aqueous selenious acid, is a white powder, insoluble or very slightly soluble in water.—The *acid mercuric salt*, formed by adding mercuric oxide to aqueous selenious acid till the neutral salt begins to separate out, then filtering and evaporating, crystallises in large prisms, longitudinally striated, having the taste of corrosive sublimate, and containing a large quantity of water. The crystallised salt melts in its water of crystallisation when heated, then solidifies, and finally sublimes unaltered. It dissolves easily in water, very slightly in alcohol; the aqueous solution is not precipitated by ammonia, and very slowly by alkaline carbonates; potash also throws down only part of the oxide. Sulphurous acid precipitates white mercurous selenite, which soon acquires a scarlet colour, from the presence of reduced selenium (Berzelius).—A *basic salt*, $3Hg''O.4Hg''SeO^3$, is obtained, according to Köhler, by boiling precipitated mercuric oxide with selenious acid. It is pale-yellow and insoluble in water.

Neutral mercurous Selenite, Hg^2SeO^3, obtained by precipitating mercurous nitrate with selenite of sodium, is a white powder, melting when heated to a dark-brown substance, which becomes lemon-yellow on cooling; at a stronger heat, it boils, and passes over in brown drops, which become amber-yellow and mostly transparent on cooling. Hydrochloric acid converts it into mercuric chloride, the selenious acid being partly reduced to the state of free selenium, and partly remaining dissolved in the liquid. The salt gives up all its acid to caustic potash. It is not soluble either in water or in aqueous selenious acid (Berzelius).—A *mercurous anhydro-salt*, $3Hg^2SeO^3.SeO^2$, is obtained, according to Köhler, as a dark, brick-red, opaque, crystalline mass, by melting the neutral salt at 180°, and raising the temperature a little higher.

Selenite of Nickel.—The *neutral salt*, obtained by precipitation, is insoluble in water, white when moist, but becomes apple-green on drying (Berzelius). According to Muspratt, on the contrary, it is precipitated, on adding selenite of potassium to sulphate of nickel, as a greenish powder, containing $Ni''SeO^3.H^2O$, which becomes white when dry.—The *acid salt* is a green gummy mass, soluble in water. (Berzelius.)

Selenites of Potassium.—Selenious acid and potash form three different salts, which are obtained by mixing the acid with potash or potassium-carbonate in the required proportions.—The *neutral salt*, K^2SeO^3, obtained by saturating carbonate of potassium with selenious acid, separates on evaporation, but not on cooling, in crystalline grains. It melts, when heated, to a yellow mass, which again becomes white on cooling; it attracts moisture from the air, and dissolves in nearly all proportions in water, but is insoluble in alcohol. It has a disagreeable taste, and strong alkaline action to test-paper.—The *acid salt*, $KHSeO^3$, crystallises with difficulty on cooling from a solution evaporated to the consistence of syrup, or from a slightly acid solution by evaporation over oil of vitriol, in feathery crystals (having a satiny lustre according to Muspratt), which unite at last to a compact mass. It slowly parts with the half of its acid when ignited. It is deliquescent, slightly soluble in alcohol.—The *hyperacid salt*, $KHSeO^3.H^2SeO^3$, is uncrystallisable and highly deliquescent. (Berzelius.)

Selenite of Silver, Ag^2SeO^3.—Selenious acid added to nitrate of silver, throws down this salt in the form of a white powder. The same salt crystallises in needles, from a nitric acid solution diluted with hot water. It is not blackened by light. Melts almost as easily as horn-silver, forming a clear liquid, which, on cooling, solidifies in a white opaque mass, friable, and having a crystalline fracture. When more strongly ignited, it gives off selenious oxide and oxygen gas, and becomes covered with metallic silver. Dissolves very sparingly in cold water, somewhat more freely in hot water, and easily in nitric acid, from which it may be precipitated by cold water (Berzelius.)

Selenites of Sodium.—The *neutral salt*, Na^2SeO^2, does not crystallise on cooling, but only by evaporation of an aqueous solution *in vacuo*; it then forms small grains, which are permanent in the air, taste like borax, and dissolve very easily in water, but not in alcohol. According to Muspratt, it forms radiated crystals, which fuse without decomposition.—The *acid salt*, $NaHSeO^3.2H^2O$ (Muspratt), crystallises during the slow cooling of a syrupy solution, in needles united together in tufts, which do not effloresce in the air, but melt when heated, with loss of their water of crystallisation, to a liquid which is yellow while hot, and solidifies, on cooling, to a white mass of a fibrous texture. At a red heat, the salt loses half its acid.—The *hyperacid salt*, $2NaH^3Se^2O^6.H^2O$ or $Na^2SeO^3.3H^2SeO^3.H^2O$ (Muspratt), first obtained by Berzelius, is prepared by dissolving the acid salt in selenious acid, and crystallises by spontaneous evaporation in needles, which are permanent in the air. It melts easily to a yellowish-red liquid, which gives off selenious oxide, leaving a residue of neutral sodium-selenite with traces of selenate. (Muspratt.)

Selenites of Strontium.—The *neutral salt*, $Sr''SeO^3$, is a white powder, infusible, and not soluble in water.—The *acid salt*, obtained like the corresponding barium-salt, separates as a milk-white amorphous crust, on evaporating the aqueous solution. It melts in the fire; swells up and evolves water at first, and then one half of its acid, so that the neutral selenite remains in a spongy form. It is nearly insoluble in cold water, and dissolves but slowly even in boiling water. (Berzelius.)

Selenites of Thallium.—The *neutral salt*, Tl^2SeO^3, is produced by oxidising selenide of thallium with nitric acid, or more easily by treating selenious acid with excess of thallium-carbonate. It has an alkaline reaction, is easily soluble in water, insoluble in alcohol and ether, and crystallises in very thin micaceous laminæ (Kuhlmann, Bull. Soc. Chim. [2] i. 330).—The *acid salt*, $TlHSeO^3$, is more soluble in water than the neutral salt, and crystallises most readily from a solution mixed with alcohol. (Kuhlmann.)

Selenites of Tin.—Stannic selenite is a white powder, insoluble in water, soluble in hydrochloric acid, and precipitated therefrom by water. When strongly heated, it first gives off water, and then the whole of its acid.

Selenites of Uranium.—*Neutral uranic selenite* is a lemon-yellow powder, which is decomposed at high temperatures, giving off oxygen and selenious oxide, and leaving uranoso-uranic oxide. It dissolves in excess of selenious acid, forming an *acid salt*, which dries up to a white, opaque, crystalline mass, soluble in water (Berzelius). According to Muspratt, the crystalline salt thus obtained is *neutral uranic selenite*, $U^2O^3.3SeO^2$.

Selenite of Yttrium is precipitated in curdy white flocks, which dry up to a white powder. It is insoluble in water and in selenious acid, and when strongly heated, first gives off water, and then the whole of its acid. (Berzelius.)

Selenites of Zinc.—The *neutral salt*, $Zn''SeO^3.H^2O$ (Muspratt), is a white powder, insoluble in water. When heated, it gives off water, and melts to a yellow transparent liquid, which on cooling forms a white mass, having a crystalline fracture. At an incipient white heat, it enters into ebullition, and is converted, with sublimation of selenious oxide, into an infusible basic salt, no longer decomposible by heat.—The *acid salt*, obtained by dissolving the neutral salt in selenious acid, is a transparent, fissured, gummy mass, easily soluble in water. (Berzelius.)

Hyperacid Salt, $Zn''H^6Se^4O^{12} = Zn''SeO^3.3H^2SeO^3$.—When clean zinc-turnings or plates of zinc are immersed in a somewhat concentrated aqueous solution of selenious acid the metal soon becomes covered with a thin red layer of reduced selenium, and a solution is formed containing hyperacid zinc-selenite, which, when the solution is evaporated to a syrupy consistence *in vacuo* over oil of vitriol, and then left at rest for about a week, separates in large yellow crystals, very much like those of neutral potassium-chromate. They are oblique rhombic prisms, having their terminal edges, and frequently also the obtuse lateral edges, replaced by planes: generally associated in twins. The salt is permanent in the air, soluble in water. The solution is colourless; has a strong sour taste; is not decomposed by acids; becomes turbid when heated, the salt being resolved into selenious oxide and neutral zinc-selenite. A crystal heated to 30° or 40° undergoes the same change, becoming white and opaque; on increasing the heat, the crystal melts, and is resolved into water which distils over, selenious oxide which sublimes, and a neutral or basic salt which remains behind. (Wöhler, Ann. Ch. Pharm. lix. 279.)

SELENITE OF ZIRCONIUM is a white powder, insoluble in water, soluble in selenious acid, decomposed by heat, leaving a residue of zirconia. (Berzelius.)

Selenic Acid, $H^2SeO^4 = H^2O.SeO^3 = \left.\begin{matrix}(SeO^2)''\\H^2\end{matrix}\right\}O^2$.—This acid, the analogue of sulphuric acid, was discovered in 1827 by Mitscherlich (Pogg. Ann. ix. 623), and has been further examined by Wohlwill (Ann. Ch. Pharm. cxiv. 162) and v. Hauer (Wien. Akad. Ber. xxxix. 299; Jahresb. 1860, p. 85).

Selenic acid (or a metallic selenate) is formed: 1. By fusing selenium, selenious oxide, or a selenite with nitrate of potassium or sodium.—2. By the action of chlorine and water, or of hypochlorous acid, on selenium, selenious acid, or selenites.—3. By heating selenious acid with peroxide of lead, peroxide of manganese, or chromate of potassium. (Wohlwill.)

Preparation.—Aqueous selenic acid is usually prepared by fusing an alkaline selenite with nitrate of potassium or sodium, precipitating the solution of the resulting alkaline selenate with a lead-salt, and decomposing the precipitated selenate of lead with sulphydric acid. According to Wohlwill, however, this process is not advantageous, because a portion of the selenate of lead obstinately resists decomposition. The following is more convenient and productive. Selenious acid is first prepared by dissolving selenium in nitric acid; and the solution, after moderate concentration, is finally evaporated down in a retort provided with a receiver, whereupon, after the excess of nitric acid and the water have been driven off, the liquid suddenly becomes briskly agitated, and a considerable quantity of the selenious acid volatilises and condenses in the receiver to a snowy mass. The solution of this sublimed selenious acid, or cupric selenite (prepared therefrom with cupric carbonate suspended in water), is treated with chlorine gas; the excess of chlorine is allowed to evaporate from the liquid by exposure to the air at the ordinary temperature; the liquid is saturated with pure cupric carbonate; and the cupric selenate contained in the liquid (filtered from unaltered cupric selenite) is separated from cupric chloride by precipitation with alcohol (which leaves the chloride in solution), or by repeated crystallisation. The cupric selenate is then suspended in a small quantity of water, and decomposed by sulphydric acid; and the filtered aqueous acid is concentrated by evaporation over the water-bath. The formation of selenic acid by oxidising selenious acid with chlorine may be used for the preparation of selenates, but not for the direct preparation of the aqueous acid, because the hydrochloric acid formed at the same time reconverts the selenic acid, unless neutralised, into selenious acid, slowly in the cold, quickly when heated. (Wohlwill.)

Von Hauer precipitates a solution of potassium-selenite with calcium-nitrate; purifies the resulting calcium-selenate by solution in water and precipitation by heat (it is less soluble in hot than in cold water); then decomposes it by boiling with excess of cadmium-oxalate and water, till the liquid is free from calcium; precipitates the cadmium from the filtered liquid with sulphydric acid; expels the excess of that acid from the filtrate by heat, and concentrates by evaporation.

Properties.—Selenic acid is a transparent colourless liquid, which in the most concentrated state boils at 280°, and has a specific gravity of 2·6. The liquid in this state is not quite pure selenic acid, H^2SeO^4, but contains a little water in addition, which cannot be driven off without further decomposition of the acid into selenious oxide, water, and oxygen. The concentrated acid resembles sulphuric acid in many of its properties. It is very hygroscopic, and its admixture with water is attended with considerable rise of temperature. The strong or dilute acid boiled with *hydrochloric acid* eliminates chlorine, and is reduced to selenious acid:

$$H^2SeO^4 + 2HCl = Cl^2 + H^2O + H^2SeO^3.$$

On the other hand, it resists the action of many reducing agents which decompose selenious acid. Thus, it is not decomposed by sulphurous or sulphydric acid, and its solution dissolves *zinc* and *iron*, with simple substitution of the metal for hydrogen, not with precipitation of selenium, as is the case with selenious acid (p. 226). The free acid precipitates *barium-salts*, even in presence of other mineral acids. By this property, taken in connection with its reduction to selenious acid, with evolution of chlorine by boiling with hydrochloric acid, selenic acid may be distinguished from all other acids.

Selenates.

Selenic acid is dibasic like sulphuric acid, and capable of forming acid as well as neutral salts. Only one acid selenate has, however, yet been prepared, viz. that of potassium, $KHSeO^4$. The neutral selenates have the composition, M^2SeO^4 or $M''SeO^4$. Many double selenates are also known, represented by the general formulæ, $M''X^2Se^2O^8$ and $M'''XSe^2O^8$, the last being analogous to the alums.

The selenates of the alkali-metals are prepared by igniting selenium, selenides, or selenites with nitrate of potassium or sodium; other selenates by dissolving metallic oxides, hydrates, or carbonates in selenic acid; the selenates of barium, strontium, and lead, which are insoluble in water, and even in nitric acid, by precipitation. The selenates correspond very closely in their properties to the sulphates, with which they are isomorphous. Most of them sustain a red heat without decomposition. Heated in a current of *hydrogen*, they are readily converted into selenides. Heated with *charcoal* or with *carbonate of sodium* in the reducing flame, they are also reduced to selenides, emitting the characteristic horseradish odour. When boiled with *hydrochloric acid*, they evolve chlorine, and leave selenious acid, from which selenium may be precipitated by sulphurous acid.

Selenate of Aluminium resembles the sulphate, and yields corresponding basic salts under similar circumstances (see Sulphates).—*Selenium-alums*, viz. $Al'''KSe^2O^8.12H^2O = \left.\begin{matrix}(Se\overset{''}{O}{}^2)^2\\ Al'''K\end{matrix}\right\}O^4.12H^2O$, and the corresponding ammonium- and sodium-salts, are obtained, by dissolving aluminium-hydrate in excess of selenic acid and neutralising with an alkaline carbonate, in monometric crystals (O with ∞O∞ and ∞O), which effloresce slightly in the air. They are all easily soluble in cold water; the sodium-salt crystallises only from very concentrated solutions, and even in presence of a considerable excess of aluminium-selenate, only in small crystals mixed with selenate of sodium (Wohlwill). The crystals of the potassium-salt have a specific gravity of 1·971. (Weber, Pogg. Ann. cviii. 615.)

Selenate of Barium, $Ba''SeO^4$, obtained by precipitation, is a white powder insoluble in water and in nitric acid, but converted into selenite and dissolved by boiling with hydrochloric acid, being thereby distinguished from the sulphate. Specific gravity = 4·67 at 22°. (Schafarik, Jahresb. 1863, p. 15.)

Selenate of Cadmium, $Cd''SeO^4.2H^2O$, prepared as above (p. 230), crystallises by cooling or spontaneous evaporation in small transparent tables, which are permanent in the air, very soluble in water, give off half their water at 100°, and the rest considerably below a red heat. (v. Hauer.)

Selenate of Calcium, $Ca''SeO^4.2H^2O$, prepared by precipitation (p. 230), separates on warming its aqueous solution, in transparent crystals, which resemble those of gypsum, and may be obtained of considerable size by slow evaporation. The dehydrated salt hardens with water, like burnt gypsum. (v. Hauer.)

Selenate of Chromium and Potassium, or *Selenic Chrome-alum*, crystallises after some time from the liquid obtained by treating a concentrated solution of acid potassium-chromate with selenic acid and alcohol at a moderate heat. (Wohlwill.)

Selenate of Cobalt, $Co''SeO^4.7H^2O$, resembles the sulphate (Mitscherlich). —*Potassio-cobaltous selenate*, $Co''K^2Se^2O^8$, resembles the corresponding nickel-salt. (v. Hauer.)

Selenate of Copper, $Cu''SeO^4.5H^2O$, prepared by dissolving copper or cupric oxide in selenic acid, or by oxidation of the selenite (p. 230), is isomorphous with the sulphate (Mitscherlich). A mixture of cupric and ferrous selenates yields, according to Wohlwill, in a number of successive crystallisations, nothing but different combinations of the form of cupric sulphate (triclinic, ii. 158); crystals having the form of ferrous sulphate (monoclinic) are obtained only when the latter is in considerable excess, as observed by Wohlwill in a mixed salt containing 3 at. Fe to 1 at. Cu. A solution of magnesium-selenate mixed with comparatively very small quantities of cupric selenate yields crystals having the form of ferrous sulphate, and containing $Cu''\overset{''}{Mg}{}^3Se^4O^{16}.28H^2O$. Selenate of zinc yields with cupric selenate a similar salt, containing $Cu''\overset{''}{Zn}{}^3Se^4O^{16}.28H^2O$.

Ferrous Selenate, $Fe''SeO^4.7H^2O$ (or $5H^2O$).—This salt, obtained by dissolving iron wire in selenic acid, and evaporating in an atmosphere of hydrogen or carbonic anhydride, crystallises with 7 at. water and the form of ferrous sulphate, only at temperatures a little above 0°. The monoclinic crystals thus obtained become opaque, and give off part of their water even on slight rise of temperature; and at temperatures not much above 5°, the salt crystallises with only 5 at. water, and in the form of cupric sulphate. (Wohlwill.)

Selenate of Lead, $Pb''SeO^4$, is obtained by precipitating selenate of sodium with nitrate of lead, as a white powder insoluble in nitric acid. Specific gravity = 6·37 at 22° (Schafarik). This salt occurs native, with selenide of lead and antimony, malachite, &c., at the Friederichsglück mine, near Hildburghausen, and at Eisfeld, in small, brittle, sulphur-yellow spheres and botryoïdal masses, cleaving distinctly in one direction. This mineral was regarded by Kersten (Pogg. Ann. xlvi. 277) as a selenite of lead; but according to H. Rose's analysis, it is a selenate of lead containing a little copper. (Dana, ii. 375.)

Selenate of Magnesium, $Mg''SeO^4.7H^2O$, exactly resembles the sulphate in form and solubility.

Selenate of Nickel, $Ni''SeO^4.6H^2O$, obtained by dissolving the carbonate in selenic acid, forms quadratic crystals, isomorphous with the sulphate containing the same quantity of water (Mitscherlich). According to v. Hauer, it crystallises from neutral solutions by spontaneous evaporation in quadratic pyramids, which give off 4 at. water at 100°, but cannot be completely dehydrated without further decomposition. A mixture of this salt and cupric selenate in nearly equivalent quantities, yields crystals having the form of ferrous sulphate. (Wohlwill.)

Nickel-potassium Selenate, $Ni''K^2Se^2O^8.6H^2O$, forms monoclinic crystals, isomorphous with the corresponding double sulphate. It cannot be dehydrated without decomposition, but gives off nearly 4 at. water at 100°, whereas the sulphate remains unaltered at that temperature. [Respecting the crystalline form, see also G. v. Rath (Pogg. Ann. cxv. 487; Jahresb. 1862, p. 215)]. The corresponding double salts formed by combination of the selenates of cobalt, magnesium, and copper with the selenates of potassium and ammonium, crystallises in the same form, are permanent in the air, more soluble than the corresponding double sulphates, and cannot be completely dehydrated without decomposition. (v. Hauer.)

Selenates of Potassium.—The *neutral salt*, K^2SeO^4, is prepared by fusing selenium or selenite of potassium, or native selenide of lead, with saltpetre, dissolving the fused mass in hot water, and leaving the concentrated solution to crystallise. The excess of nitrate then crystallises out first, and afterwards the selenate, in crystals exactly resembling the neutral sulphate. It deflagrates on glowing coals like saltpetre, and is equally soluble in hot and in cold water (Mitscherlich).—The *acid salt*, $KHSeO^4$, exactly resembles the acid sulphate. (Mitscherlich.)

Selenate of Silver, Ag^2SeO^4, prepared by dissolving silver in selenic acid, agrees with the sulphate in form and properties.

Selenate of Sodium, Na^2SeO^4, is prepared like the potassium-salt, and crystallises from aqueous solution above 40° in anhydrous crystals; at lower temperatures, or by spontaneous evaporation, in crystals containing $Na^2SeO^4.10H^2O$, exactly resembling those of Glauber's salt, and exhibiting, like the latter, a maximum solubility at about 33°. (Mitscherlich.)

Selenate of Thallium, Tl^2SeO^4, prepared by dissolving the metal or its carbonate in selenic acid, crystallises in long, white, prismatic needles, isomorphous with sulphate of potassium, sparingly soluble in cold water, insoluble in alcohol and in ether. (Kuhlmann, Bull. Soc. Chim. 1864, i. 330.—Oettinger, Zeitschr. Ch. Pharm. 1864, p. 440.)

Selenate of Zinc, $Zn''SeO^4.7H^2O$, is isomorphous with the sulphate. According to Mitscherlich, it crystallises also with 2 at. and 6 at. water, the dehydrated salt separating at temperatures above 30°, the hex-hydrate between 20° and 15°. The solution mixed with ferrous sulphate deposits, according to Wohlwill, crystals having the form of cupric sulphate. When a solution of zinc-selenate is mixed with cupric selenate, the former being in considerable excess, the crystals which first separate have the form of cupric sulphate; and it is only the last that exhibit the quadratic form of zinc-selenate (Wohlwill).—*Selenate of zinc and thallium*, $Zn''Tl^2Se^2O^8.6H^2O$, crystallises in monoclinic prisms, isomorphous with magnesio-potassic sulphate. (G. Werther, Bull. Soc. Chim. 1865, i. 60.)

SELENIUM, OXYCHLORIDE OF. $SeCl^2O = SeCl^4.SeO^2$. *Selenacichlorid.* (R. Weber, Pogg. Ann. cviii. 615.)—Produced by distilling tetrachloride of selenium over selenious oxide gently heated in a sealed tube: also in the decomposition of the tetrachloride by a small quantity of water, and is therefore always present in the liquid resulting from the deliquescence of the tetrachloride, in damp air. It is a slightly yellowish liquid, having a specific gravity of 2·44, boiling at about 220°, fuming in damp air, and easily decomposed by water into hydrochloric and selenious acids.

SELENIUM, SULPHIDES OF. Two of these compounds are known, analogous in composition to selenious oxide and the unknown selenic oxide. The disulphide or selenious sulphide, SeS^2, is produced by fusing 1 at. selenium with 2 at. sulphur; also by the action of sulphydric acid on a solution of selenious acid.* The latter method yields it as a bright yellow precipitate, becoming darker when dry. It softens at 100°, melts at a somewhat higher temperature, and when more strongly heated, boils, distils over, and solidifies on cooling to an orange-yellow mass resembling orpiment. Alkalis dissolve the sulphur from it easily and completely, together with a small quantity of selenium. Alkaline sulphydrates dissolve it completely. (Berzelius.)

The trisulphide or selenic sulphide, SeS^3, is produced by fusing 1 at. selenium with 3 at. sulphur. It is a brick-red, fusible, volatile solid, soluble without residue in alkaline hydrates and sulphydrates. (Berzelius.)

SEMECARPUS. The almonds of *Semecarpus Anacardium*, L. (*Anacardium orientale*), an East Indian plant, contain a small quantity of sweet oil; the pericarp contains 32 per cent. of a a vesicating oil of specific gravity 0·991, easily soluble in ether, blackening on exposure to the air. (J. Lepire, J. Pharm. [3] xl. 16.)

SEMEN CINÆ. Syn. with WORMSEED.

SEMEN COCCOGNIDII. Mezereum-seeds (iii. 1010).

SEMIBENZIDAM. This name was given by Zinin to a compound produced by the action of sulphide of ammonium on dinitrobenzene; probably impure α-phenylene-diamine (iv. 480).

SEMINAPHTHALIDAM, SEMINAPHTHALIDINE. See the next article.

SEMINAPHTHYLAMINE. $C^{10}H^8N^2$ = AMIDONAPHTHYLAMINE, $C^{10}H^8(NH^2)N$ or NAPHTHYLENE-DIAMINE $\left.\begin{matrix}(C^{10}H^6)''\\H^4\end{matrix}\right\}N^2$; also called *Seminaphthalidine, Seminaphthalidam*, and *Azonaphthylamine*. (Zinin, Ann. Ch. Pharm. lii. 362; lxxxv. 329.)—A base produced by the action of sulphydrate of ammonium on dinitronaphthalene (iv. 15). To prepare it, dinitronaphthalene is dissolved in alcohol saturated with ammonia, and the crimson solution is saturated with sulphydric acid, then boiled, whereupon it deposits a large quantity of sulphur; afterwards, mixed with water, boiled again, and filtered quickly at the boiling heat. On cooling it deposits a large quantity of naphthylene-diamine in thin, shining, copper-coloured needles, which may be rendered colourless by alternate crystallisation from alcohol and water.†

Naphthylene-diamine crystallises from alcohol in long shining needles, slightly soluble in water, very soluble in alcohol and ether; forming brownish-yellow solutions, which quickly become darker-coloured and turbid on exposure to the air. In the dry state it may easily be kept unaltered. It melts at 160°, and when heated above 200°, boils and distils, with partial decomposition and carbonisation. It dissolves in strong sulphuric acid, forming a dark-violet solution, which remains unchanged for months if left to itself; but, on addition of water, is immediately transformed into a reddish-white crystalline mass. The alcoholic solution of the base is decolorised by aqueous acids, forming crystalline magmas, whence it is precipitated by ammonia without alteration.

Salts of Naphthylene-diamine.—This base is diacid, uniting with 2 at. of a monatomic and 1 at. of a diatomic acid. The *hydrochlorate*, $C^{10}H^{10}N^2.2HCl$, is prepared by dropping rather strong hydrochloric acid into a cold concentrated solution of naphthylene-diamine in a vessel externally cooled. A magma of shining scales is thus obtained, which must be washed with alcohol. The salt cannot be sublimed. Its aqueous solution becomes coloured on exposure to the air. The *chloromercurate* crystallises in broad very soluble laminæ.—The *chloroplatinate*, $C^{10}H^{10}N^2.2HCl.Pt^{iv}Cl^4$, is a yellow-brown sparingly soluble powder.

The *sulphate*, $C^{10}H^{10}N^2.H^2SO^4$, is obtained by treating an alcoholic solution of the base with dilute sulphuric acid, as a white powder, slightly soluble in water and in alcohol, whence it crystallises in colourless scales.—The *phosphate* forms shining scales, more stable than the sulphate, slightly soluble in water and in alcohol, and crystallising therefrom without alteration.

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* According to H. Rose, however, the precipitate thus formed is only a mixture of selenium and sulphur.

† The red colour of the first crop of crystals arises from a foreign substance much more soluble in alcohol than naphthylene-diamine itself. This coloured body crystallises from water in very slender lustreless needles, which, when heated in a tube, melt to a red liquid, and then distil with partial decomposition.

The *oxalate* is a white crystalline powder, slightly soluble in water, still less soluble in alcohol and in ether. A solution prepared at the boiling heat deposits it on cooling, in shining scales.—The *tartrate* crystallises in radiate groups of slender needles, moderately soluble in water and in alcohol, less soluble in ether. It decomposes in solution, but is more permanent in the dry state.

SEMI-OPAL. A variety of opal, translucent at the edges only (iv. 204).

SENARMONTITE. The monometric variety of antimonious oxide, Sb^2O^3 (i. 323), occurring at Sensa, in the province of Constantine, Algeria, and at Perneck near Malackza in Hungary, in regular unmodified octahedrons, and in masses with granular structure. Hardness = 2 to 2·5. Specific gravity = 5·22 to 5·3. It has a greyish or yellowish colour, and resinous lustre inclining to subadamantine; transparent to translucent.

SENECA OIL. American petroleum, so called because it was collected and sold by the Seneca Indians.

SENEGAL GUM. See GUM (ii. 954).

SENEGIN or **SENEGUIN.** See SAPONIN (p. 193).

SENNA. A purgative drug consisting of the leaves of *Cassia acutifolia*, a shrub indigenous in Egypt, Nubia, Arabia, and India, and *Cassia obovata*, indigenous in Egypt, Tripoli, and Syria. It has been examined by several chemists, chiefly with the view of extracting the active principle, but the results are by no means accordant. Lassaigne and Feneulle (J. Pharm. x. 58) attribute the purgative action to a bitter uncrystallisable substance, soluble in water and alcohol, insoluble in ether, which they denominate cathartin (i. 817). Bley and Diesel (Arch. Pharm. [2] lv. 257), obtained from senna-leaves a similar substance, together with a yellow resin, chrysoretin (i. 960), soluble in ether, and resembling chrysophanic acid, probably a mixture of that acid with other substances. According to Martius (*Monographie der Sennesblätter*, Leipzig, 1857), senna contains chrysophanic acid (i. 258) together with two brown substances, similar to or identical with the aporetin and phæoretin of rhubarb; also margarin; he regards the chrysophanic acid as the active principle. Sawicki, on the other hand (*Dissertatio inauguralis*, Dorpati, 1857), doubts the correctness of this view, inasmuch as the purgative principle of senna is extracted by water much more easily than by alcohol, whereas chrysophanic acid is nearly insoluble in water, but dissolves in alcohol, by which indeed it is extracted from rhubarb. Wiggers endeavours to explain this contradiction by supposing that the chrysophanic acid in senna is for the most part combined with bases, and in that state insoluble in alcohol, whereas in rhubarb it exists chiefly in the free state.

Martius found in senna-leaves from *Cassia acutifolia* from 9 to 12 per cent. of ash. The composition of the ash in 100 pts. is, according to Martius (*a* and *b*) and Schreiber (*c*), as follows:—

	K^2O	Na^2O	MgO	CaO	$Fe'''PO^4$	P^2O^5	SiO^2	Cl	SO^3	CO^2	Sand and charcoal.
Alexandrian (*a*)	16·58	1·08	7·46	35·92	0·32	. .	2·00	0·35	2·95	24·75	6·97
East (*b*)	11·20	8·50	6·10	36·28	5·70	. .	4·06	0·70	3·52	21·10	3·69
Indian (*c*)	13·47	1·24	0·85	35·36	1·50	3·82	14·49	3·81	1·45	23·57	

SEPEERINE, or **SEPIRINE.** Syn. with SIPEERINE.

SEPIA. A dark-brown pigment prepared from a black juice, which is secreted by certain glands of the cuttle-fish (*Sepia officinalis*, *Sepia Loligo*, &c.), and ejected by the animal to darken the water when it is pursued. One part of the juice is capable of making 1000 parts of water nearly opaque. The juice, when dried, yields a black mass, which, according to Prout, consists of 78 per cent. black pigment or melanin, 10·40 calcium-carbonate, 7·00 magnesium-carbonate, 2·16 alkaline sulphates and chlorides, and 0·84 mucus. The black pigment may be isolated by boiling the black mass successively with water, hydrochloric acid, and dilute solution of ammonium-carbonate. It is a black, inodorous, and tasteless substance, quite insoluble in water, alcohol, and ether, but, remaining suspended in water for a very long time, its deposition may, however, be accelerated by addition of acids or sal-ammoniac. It dissolves in warm caustic potash solution, forming a dark-brown solution, from which it is precipitated by sulphuric and hydrochloric acid, but not by nitric acid. It dissolves also in ammonia, but not in alkaline carbonates.

The pigment is prepared by saturating the dried native sepia with a little caustic lye, then adding more lye, boiling the liquid for half an hour, filtering, precipitating with an acid, washing the precipitate, and drying it at a gentle heat. It is of a dark-brown colour and fine grain.

Os sepiæ, *Meerschaum*, or *White Fish-bone*, is the calcareous shield or shell on the back of the cuttle-fish. It consists of two layers: the upper thin, but very compact, while the lower is thicker but porous. The upper layer contains, according to John, 80 per cent. calcium-carbonate with traces of phosphate, 9 gelatinous substance, insoluble in water and in cold lime-water, 4 water, and traces of magnesia. The lower layer contains 85 calcium-carbonate, with traces of potash, 4 gelatinous matter, and 4 water, with traces of magnesia. Forchhammer found in *Os sepiæ* 0·10 per cent. magnesium-carbonate.

Os sepiæ is used as tooth-powder, for polishing, and for modelling for fine gold articles; it was formerly used as an internal remedy in cases of goître. (Handw. d. Chem. vii. 839.)

SEPIOLITE. Syn. with Meerschaum (iii. 864).

SEPIRINE. Syn. with Sipeerine.

SEPTARIA. Calcareous concretions intersected by veins of calcspar, which, when calcined and ground, form an excellent hydraulic cement.

SERBIAN. Syn. with Miloschin.

SERICIC ACID. Syn. with Myristic acid.

SERICIN (from *Serica*, silk). A name proposed by Schlossberger (Ann. Ch. Pharm. cx. 245) for the fibroïn of silk and of gossamer-threads (ii. 644), which, according to him, are identical, but different from the organic matter of sponges, for which he retains the name fibroïn.

The name sericin was formerly also applied to myristin, the glyceride of myristic acid (iii. 1072), on account of its silky aspect.

SERICITE. A mineral occurring in a schist of the Taunus range in Western Germany. It has a greenish or yellowish-white colour, silky lustre; hardness = 1; specific gravity = 2·897. Foliated in one direction, the plates being undulated. Exfoliates strongly before the blowpipe, and melts on the edges with a bright light, forming a greyish enamel. Decomposed slowly by hydrochloric acid. Contains, according to List (Ann. Ch. Pharm. lxxxi. 193), 1·22 per cent. fluorine, 0·31 phosphoric anhydride, 1·59 titanic anhydride, 50·00 silica, 23·65 alumina, 8·07 ferrous oxide, 0·93 magnesia, 0·63 lime, 9·11 potash, 1·75 soda, and 3·11 water. It is distinguished from potash-mica by its small amount of alumina. List regards it as identical with Damourite (ii. 303).

SERICOLITE. *Satin spar. Atlasspath.* A mineral from Alston Moor, in Cumberland, formerly regarded as a fibrous arragonite, but belonging, according to G. Rose's latest investigations, not to arragonite, but to calcspar. (Handw. d. Chem. vii. 841.)

SEROLIN. This name was given by Boudet (J. Pharm. xix. 291), to a fat which he obtained by treating dried blood-serum with ether or boiling absolute alcohol, and evaporating the solution. According to Boudet, it is quite destitute of crystalline structure; according to Verdeil and Marcet (J. Pharm. [3], xx. 89), it crystallises from boiling alcohol in nacreous laminæ. When once separated from blood-serum, it no longer dissolves in that liquid. According to Gobley (*ibid.* xxi. 241), the so-called serolin is not a pure substance, but a mixture of several fats of different melting points.

SEROUS FLUID. The serous cavities of the body (viz., peritoneal, pleural, pericardial, &c.) contain a small quantity of fluid, called serous fluid, from its general resemblance to the serum of blood. A similar fluid, found in blisters, in cuticular vesicles, and in the interstices of connective tissue, is more generally called 'lymph.' Under certain morbid conditions, the quantity of serous fluid in various parts becomes very much increased, giving rise to the various forms of dropsy.

There is reason to believe that in health, and during life, serous fluid, whether from peritoneum, pericardium, pleura, or vagina testis, possesses, like blood, the property of coagulating at the ordinary temperature when removed from the body; in other words, that it contains both the elements necessary for the formation of fibrin. When, however, serous fluid is not removed from the body until several hours after death, the power of spontaneous coagulation has either become very much lessened or entirely disappeared. When the quantity has been abnormally increased, as in dropsies, the spontaneous coagulation is often absent. In most of these cases, if not in all, coagulation (formation of fibrin) can be brought about by the addition of blood, or of a solution of globulin (fibrinoplastin), showing that one element of fibrin (fibrinogen) still remains. These fibrinary elements may be separated by saturating the fluid with sulphate of magnesia and filtering, in which process they are retained on the filter, and may be readily dissolved in water; or by diluting the fluid with 5 or 10 times its bulk of water, and either passing carbonic anhydride through it, or cautiously adding a few drops of dilute acetic acid, collecting the precipitate, and dissolving it in a dilute solution of a neutral alkaline salt, or by the aid of a few drops of an extremely dilute solution of caustic alkali. Serous fluid, when freed by filtration from fibrin (if it has been formed), epithelial scales, &c., is clear, slightly fluorescent, of a yellow or golden colour, and distinctly alkaline, with a specific gravity varying from 1·005 to 1·030. It contains, besides the fibrinary elements, albumin, fats, cholesterin (protagon?) sugar (or an unfermentable substance reducing cupric salts), urea, uric acid, and frequently xanthine. According to Naunyn (Arch. Anat. Phys. 1865, p. 166), creatine, creatinine, and hippuric acid are never found in it. The inorganic salts are nearly the same as those of blood-serum. In serous fluid which had become purulent, Naunyn found leucine, tyrosine (guanine), and xanthine, but no urea or uric acid. In 1000 cc. of peritoneal fluid (ascites), Planer found 95·2 cc. free, and 48·8 cc. combined, carbonic anhydride, 21·0 cc. nitrogen, and 0·14 cc. oxygen (measured at 0° and 76 mm.). The following table shows the composition of serous fluid from various sources:—

	Hydrocele. (W. Müller.)	Hydrocele. (W. Müller.)	Pleura. (C. Schmidt.)	Pleura. Morbus Brightii. (F. Hoppe.)	Pericardium. Gorup-Besanez.	Peritoneum ascites. (Vogel.)
Specific gravity	1·021	1·022				
Water	940·155	934·079	936·0	957·59	955·13	946.0
Solids	59·845	65·921	64·0	42·41	44·87	54·0
Albumin	43·855	51·758	53·4	27·82	25·49	33·0
Fat and extractives	7·748	4·942	3·0		12·69	13·0
Salts	8·242	9·221	7·4		6·69	8·0

	Peritoneum. Cirrhosis. (Hoppe.)	Peritoneum. Morbus Brightii. (Hoppe.)	Peritoneum. Cirrhosis. (Redtenbacher.)	Œdema of Feet. Morbus Brightii. (Hoppe.)	Aqueous Humour of Calf. (Lohmeyer.)	Tears. (Lerch.)
Specific gravity	1·094		1·018			
Water	984·59	963·68	947·17	982·17	986·870	982·0
Solids	15·50	32·32	52·83	17·83	13·130	18·0
Albumin	6·17	16·11	42·05	3·64	1·223	5·0
Fat and extractives	1·25	5·27	3·02	5·19	4·210	
Salts	8·08	10·94	7·76	9·00	7·697	13·2 (NaCl 13·0)

Hoppe (Schmidt, A. Archi. Anat. Phys. 1861, p. 713) estimated, by means of the polarization apparatus, the percentage of albumin in 38 cases to be as follows:—Hydrocele: mean of 17 cases 5·6; pericardium: mean of 11 cases 2·0, case of general dropsy 0·7, case of typhus 4·0; peritoneum: mean of 5 cases 1·3, case of general dropsy 0·2; pleura: hydrothorax 1·6, pleurisy 4·2.—*Aqueous humour*, which may be considered as a serous fluid, contains globulin (fibrinoplastin) and urea. The *tears* contain mucus in addition to albumin, and are remarkable for their large amount of chloride of sodium.

M. F.

SERPENTARIN, or *Aristolochin*. The bitter principle of the root of *Aristolochia serpentaria*.

SERPENTINE. *Ophite*, *Ophiolite*: including *Picrolite*, *Marmolite*, *Metaxite*, *Williamsite*, *Bowenite*, *Chrysotil*, *Sparkling Asbestos*, *Baltimorite*, *Antigorite*.—A mineral, consisting essentially of hydrated magnesium-silicate, the magnesium being replaced, to a variable but never very considerable amount, by iron (ferrosum).

Serpentine usually occurs massive, sometimes forming entire mountain masses, also granulous, impalpable, fibrous, or foliated; sometimes in crystals, apparently trimetric; but these are not true crystals of serpentine, but pseudomorphs after chrysolite. From variations in the proportions of its constituents, and its mode of occurrence, and from admixture with other minerals, it exhibits numerous varieties, some of which have been regarded as distinct species: *e.g.* Picrolite, Williamsite, Bowenite, Antigorite, Baltimorite, &c.

Serpentine has usually a leek-green or blackish-green colour, sometimes nearly white, becoming yellowish-grey on exposure; it is often spotted or veined, as in verd antique marble, which consists of serpentine veined with calcic carbonate. Chrome-iron is also frequently disseminated through serpentine, giving it a mottled appearance like the skin of a snake, whence its name. Streak white, slightly shining. Lustre resinous or greasy, but of low intensity: the fibrous variety, chrysotil, has a silky lustre. Translucent to opaque. Hardness = 3 – 4. Specific gravity = 2·507 – 2·591. Fracture conchoïdal or splintery. Sectile. Thin fibres flexible.

Serpentine heated in a glass tube gives off water and often blackens. Before the blowpipe it mostly burns white, and melts with difficulty on the sharpest edges. When pulverised it dissolves in hydrochloric, and more readily in sulphuric acid.

Some serpentines contain alumina, others are free from it. In the following analyses the two classes are distinguished, and in each class the analyses are arranged according to increasing amount of iron:—

I. Serpentines not containing Alumina:—*a.* Serpentine from Gulsjö in Wermland, Sweden (Mosander)*.—*b. Bowenite,* from Smithfield, Rhode Island: green; fine-grained; specific gravity = 2·594 — 2·787 (Smith and Brush).—*c.* Serpentine from Sala, in Sweden (Lychnell).—*d. Williamsite,* from Westchester, Chester County, Pennsylvania: green, laminated; specific gravity = 2·29 — 2·64; accompanied by common serpentine and chrome-iron (Smith and Brush).—*e. Chrysotil,* from Newhaven, Connecticut: specific gravity = 2·49 (Brush).—*f. Picrolite,* from Reichenstein, in Silesia: greenish-grey (List).—*g. Marmolite,* from Blandford, Massachusetts (Shepard).—*h.* Serpentine, from Windish Mattrey, Kaiserthal, in the Tyrol: conchoïdal; specific gravity = 2·59; (Gilm).—*i.* Serpentine, from Kynance Bay, in Cornwall (Houghton):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Carbonic anhydride	0·89	. .	1·03						
Silica . . .	42·34	42·29	42·16	42·10	44·05	44·61	40·08	43·07	38·29
Magnesia . .	44·20	42·30	42·26	41·50	39·24	39·75	41·40	38·05	34·24
Ferrous oxide .	. .	1·21	2·03	2·43	2·53	2·63	2·70	5·71	13·50
Nickel oxide .	. .	. .	. .	0·45					
Water . .	12·38	12·96	12·33	12·70	13·49	12·57	15·67	12·91	12·09
	99·81	98·76	99·81	99·18	99·31	99·56	99·85	99·74	98·12

II. Serpentines containing Alumina:—*a. Chrysotil* in compact serpentine, from Abbotsville, New Jersey: yellowish-white (Reakirt).—*b. Marmolite* from New Jersey (Garrett).—*c. Williamsite* from Westchester (Hermann).—*d. Chrysotil* (sparkling asbestos) from Reichenstein in Silesia (v. Kobell).—*e.* Noble serpentine from Fahlun (Lychnell).—*f.* Serpentine from the Serpentine Peak, Ate Chonire, between Breona and Chombaira in the Valais: massive; blackish-green (Schweizer).—*g. Antigorite* from the Antigoria Valley near Domo d'Osola (Brush).—*h. Radiated Picrolite* from the Taberg, Sweden (Lychnell).—*i.* So-called *asbestos* from the compact serpentine of Zöblitz in Saxony: specific gravity = 2·60 — 2·65 (C. Schmidt).—*k. Baltimorite* from Bare Hills, Maryland (Thomson):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*k.*
Carbonic anhydride . .	. .	. .	. .	. .	3·42	. .	. .	1·73		
Silica	42·62	42·32	44·50	43·50	41·95	44·22	41·58	40·98	43·70	40·95
Alumina	0·38	0·66	0·75	0·40	0·37	1·36	2·60	0·73	2·76	1·50
Magnesia	42·67	42·23	39·71	40·00	40·64	36·41	36·80	33·44	29·96	34·75
Ferrous oxide . . .	0·27	1·28	1·39	2·08	2·22	4·90	7·22	8·94	10·03	10·05
Nickel-oxide . . .	. .	. .	0·90							
Soda	. .	. .	. .	. .	. .	. .	. .	. .	1·98	
Water	14·25	13·80	12·75	13·80	11·68	13·11	12·67	12·86	12·27	12·60
	100·19	100·29	100·00	99·78	100·28	100·00	100·87	98·68	100·70	99·85

All these analyses may be approximately represented by the formula $3Mg''O.2SiO^2.2H^2O$, or $Mg''SiO^3.\overset{''}{M}g^2SiO^4.2H^2O$, the magnesium being more or less replaced by iron, and the silica in the serpentines of the second class partly replaced by alumina. The calculated composition of a non-aluminiferous serpentine is, according to this formula, 44·14 per cent. silica, 42·97 magnesia, and 12·89 water.

Serpentine is frequently a result of pseudomorphic changes. Hornblende, augite, chrysolite, garnet, spinel, mica, and many other minerals occur thus altered. Rose has found that some of the supposed crystals of serpentine are partly chrysolite, the change not having been complete.

Precious or noble serpentines come from Fahlun and Gulsjö in Sweden, the Isle of Man, the neighbourhood of Portsey in Aberdeenshire, Corsica, Saxony, and Siberia, and many localities in the United States of America. Serpentine occurs in crystals at Lake Auschkal, in Miask, Borsovka, &c. Common serpentine occurs at Lizard's Point in Cornwall, and many other places.

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* For references, see *Rammelsberg's Mineralchemie*, p. 531.

Serpentine admits of a high polish, may be turned in a lathe, and is used for making vases, boxes, and various ornamental articles; it may also be made available as a source of magnesia. (Dana, ii. 284.)

SERPENTINE-ASBESTOS. *Chrysotil.* (See the last article.)

SERPENTINE-DOLOMITE. Mixtures of serpentine and dolomite. For these and similar mixtures of serpentine with calcspar, magnesite, &c., T. S. Hunt (J. pr. Chem. lxxiv. 150) proposes the name ophiolite, distinguishing them as calcitic, dolomitic, magnetitic, ophiolitic, &c.

SERPENTINITE, from Reichenstein in Silesia, appears to be a soft, somewhat steatitic alteration of serpentine.

SERRATULA TINCTORIA. *Sawwort.* A composite plant of common occurrence, formerly cultivated for its yellow dye, which, however, is now seldom used, as it is inferior to weld.

SERUM OF BLOOD. See Blood (i. 608).

SERUM OF MILK. *Whey.* The opalescent liquid containing milk-sugar and various salts, which separates when milk is curdled by the action of acids, rennet, &c.

SESAME-OIL. A fatty oil obtained from the seeds of *Sesamum orientale*, a plant indigenous in India, and cultivated in other warm countries. According to Lefort, it has the composition $C^{16}H^{18}O^2$, and forms with bromine and chlorine the substitution-products $C^{16}H^{17}BrO^2$ and $C^{16}H^{17}ClO^2$. It is a non-drying oil, of yellowish colour, inodorous, and having a slight taste of hemp. Specific gravity = 0·9230 at 15°, diminishing, with rise of temperature, by 0·00075 for each degree centigrade. At $-5°$ it solidifies to the consistence of palm-oil. It is used for burning in lamps, for soap-making, and for adulterating olive-oil; in India as an article of food.

SESLERIA CŒRULEA. *Blue Moor Grass.*—This grass, growing on the mountains of England and Scotland, contains, according to C. Sprengel (J. f. techn. Chem. x. 51) in 100 pts.: 55 pts. water, 10·1 matter soluble in water, 19·0 soluble in dilute potash, 0·8 wax and resin, 14·9 (?) iron. 100 pts. of the dried plant yield 5·67 pts. ash (Sprengel), 4·6 pts. (Hruschauer, Ann. Ch. Pharm. lix. 204). The ash contains in 100 pts., after deduction of carbonic anhydride:

K^2	Na^2O	CaO	MgO	Al^2O^3	Fe^2O^3	Mn^2O^3	SO^3	P^2O^5	SiO^2	$NaCl$	
14·8	4·3	22·6	trace	2·5	1·2	0·6	5·5	3·7	44·8	trace	(Sprengel)
9·2	8·8	17·2	6·4	. .	5·9	. .	5·9	15·5	27·3	3·8	(Hruschauer.)

SESQUI. Prefix, denoting one and a half: *e.g.* Fe^2O^3 or $FeO^{1\frac{1}{2}}$, sesquioxide of iron.

SEVERITE. An argillaceous mineral from Saint-Sevêre in France, where it occurs in masses below tertiary gypsum. It contains, according to Pelletier, 50 per cent. silica, 22 alumina, and 26 water, and appears to be related to halloysite and lenzin. But it is very difficult to determine whether a mineral of this character is a distinct species or a mixture. Another mineral from Saint-Sevêre, exactly resembling severite in physical characters, was found by v. Hauer to contain 44·42 per cent. silica 36·00 alumina, 18·4 water, and 0·65 lime. (Handw. d. Chem. vii. 844.)

SEXANGULITE. Breithaupt's name for sulphide of lead, occurring at Berncastel in hexagonal forms, as a pseudomorph after pyromorphite. (Jahresb. 1862, p. 709; 1863, p. 796.)

SEYBERTITE. Syn. with Clintonite (i. 1026).

SHEA-BUTTER. A vegetable fat obtained in West Africa from the nuts of *Bassia Parkii.* The nuts are shelled, and the kernels, which consist almost wholly of fat, are boiled with water and pressed. Shea-butter is greenish-white, solid at common temperatures, softens at 35°, melts at 43°; dissolves for the most part in boiling alcohol, and crystallises on cooling; also in ether, and crystallises therefrom. By saponification and decomposition of the soap, it yields an acid which separates in pearly scales, melts at 61·1°, and forms a silver-salt containing 54·71 per cent. carbon, 8·98 hydrogen, 27·83 silver, and 8·48 oxygen (Thomson and Wood, Phil. Mag. [3], xxxiv. 350). According to Oudemanns (J. pr. Chem. lxxxix. 205), it yields 29·7 per cent. oleic acid, 70·3 stearic acid (melting at 69°), but no palmitic acid or any other acid of the series $C^nH^{2n}O^2$, of lower atomic weight. Similar results have been obtained by Ruff. (*Gmelin's Handbook*, xvi. 334.)

SHELLAC or **SHELL-LAC.** Lac purified by melting and straining (iii. 451). Seed-lac or grain-lac contains, according to John, two resins soluble in alcohol, and an insoluble resin (laccin), besides colouring matter, a bitter principle, and impurities. Shellac contains two resins and a wax, but no laccin. It is of yellowish-brown, brown, or black colour, translucent, hard, with a shining conchoïdal fracture, and has, according to Brisson, a specific gravity of 1·139. It dissolves easily in hydrochloric acid, acetic acid, potash, soda, and borax, but not in ammonia (Hatchett); with moderate facility in wood-spirit, and is precipitated therefrom by water. It is perfectly soluble in amylic alcohol and valerianic aldehyde, moderately soluble in valerianic acid, slightly in amylic valerate (Trautwein). It dissolves partially in cold creosote (Reichenbach), but slightly in boiling rock-oil (Sunssure) and in benzene, though benzene mixes with its solution in methylic or ethylic alcohol (Mansfield); in 1⅓ pts. of acetone, forming a thick oily varnish. (Wiederhold.)

The bleaching of shellac on the large scale is effected by chlorine or its compounds, but the best material for the purpose is bone-charcoal (Elsner), especially bone-black, purified by means of hydrochloric acid, and not subsequently dried (Kraut). A perfectly white shellac, having a silky lustre, and completely soluble in alcohol, is obtained by the following process: 25 pts. of shellac are dissolved in 600 pts. of water containing 10 pts. of soda; and the solution is mixed with dilute hypochlorite of sodium (prepared from 30 pts. chloride of lime), and then with hydrochloric acid, as long as the precipitate redissolves. It is then exposed to the sun for a day or two, filtered, mixed with sulphite of sodium, and precipitated by hydrochloric acid. (*Gmelin's Handbook*, xvii. 420.)

SHEPARDITE. This name is given by W. Haidinger to the small brown striated prisms, consisting essentially of a sulphide of chromium, occurring in the meteorite of Bishopsville in South Carolina (iii. 981). Shepard, who examined this mineral, called it *Schreibersite*; but this name belongs to the phosphide of iron and nickel occurring in meteoric iron.

SIBERITE. Syn. with Rubellite or Red Tourmalin. (See TOURMALIN.)

SICCATIVES. Varnishes added to oil-paints to make them dry quickly. They are prepared by boiling linseed-oil with metallic oxides, or salts. Formerly litharge, minium, umber, and gypsum were employed for the purpose, but more recently the oxides and salts of manganese have come into use; they produce rapidly drying siccatives, and when added to zinc-white, do not introduce any substance that can be blackened by sulphuretted hydrogen. A mixture of equal parts of manganous sulphate and acetate with an equal quantity of zinc-sulphate and 97 pts. zinc-white added in the proportion of one-half to one per cent. to the zinc-oxide with which the oil-colour is to be prepared, is said to effect the drying of the paint in 12 hours. A similar mixture is the *siccative zumatique de Barruel*, which, according to Bolley (Dingl. pol. J. cxli. 398), is made by mixing from 5 to 6 pts. of borous manganate with 95 pts. of zinc-white, and adding to zinc-white colours in the proportion of 2½ per cent. (Handw. d. Chem. vii. 846.)

SIDA CARPINIFOLIA. The leaves and flowers of this plant are used medicinally in Brazil for the same purposes as mallow.

SIDERITE. A name applied to native ferrous carbonate or spathic iron-ore, to pharmacosiderite or cube-ore (ferric arsenate, ii. 171), and to a blue variety of quartz from Golling, near Salzburg.

SIDEROCHALCITE. Syn. with Abichite, one of the forms of native cupric arsenate.

SIDEROCONITE. A variety of calcspar, coloured yellow or brown by ferric hydrate.

SIDERODOTE. Breithaupt's name for a calcareous iron-spar from Radstadt in Salzburg: specific gravity = 3·41.

SIDEROFERRITE. This name is given by Bahr (J. pr. Chem. liv. 194) to native iron found in a petrified tree on a floating island in the Ralanger Lake in Smaland, Sweden. The tree is converted into ferrous hydrate (bog iron-ore), and the iron forms small grains, probably resulting from the reduction of an iron-salt. The iron is porous, and has a specific gravity of 6·248 to 6·497, increased by hammering to 6·626.

SIDEROGRAPHITE. A native iron from North America, containing a somewhat considerable quantity of carbon. (Torrey, *Glocker's Grundiss d. Min.*, p. 342.)

SIDEROMELANE. A mineral from the palagonite-tufa of Iceland, resembling obsidian in colour, lustre, and fracture: specific gravity = 2·531. It differs from true palagonite (iv. 324) in not being decomposible by hydrochloric acid. Contains 45·10 per cent. silica, 13·73 alumina, 18·52 ferric oxide, 8·10 lime, 3·21 magnesia, 2·33 soda, 0·95 potash, 0·35 water, and 6·52 residue (= 98·81). The oxygen-ratio in the protoxides, sesquioxides, and silica is 1 : 3 : 6, the same as in labradorite. (Sartorius v. Waltershausen, *Vulkanische Gesteine*, p. 179.)

SIDEROPHARMACOLITE. Syn. with ABICHITE.

SIDEROPLESITE. Breithaupt's name for a variety of mesitin-spar $(Mg ; Fe)''CO^3$, found at Pöhl in the Saxon Voigtland, containing 2 at. $Fe''CO^3$ to 1 at. $Mg''CO^3$. Angle, R : R = 107° 6′; specific gravity = 3·616 to 3·660 (Breithaupt, Sill. Am. J. [2] xxvi. 348). It is also found at Traversalla, in Piedmont, and at Böhmsdorf, near Schleiz. An allied mineral from Mitterberg in the Tyrol was found by Köhn to contain 4 at. $Fe''CO^3$ to 1 at. $Mg''CO^3$. (Jahresb. 1858, p. 733.)

SIDEROSBOLE. A name applied by Breithaupt to a variety of bole, having a higher specific gravity (= 3·24) than ordinary bole, which he attributes to the presence of a larger proportion of iron.

SIDEROSCHISOLITE. A ferroso-ferrous silicate, occurring at Conghonas do Campo in Brazil, in hexagonal crystals, closely resembling cronstedtite in colour and other physical characters, and in its behaviour before the blowpipe. The analysis of a very small specimen by Wernekink (Pogg. Ann. i. 387), gave 16·3 per cent. silica, 75·5 ferroso-ferric oxide, 4·1 alumina, and 7·3 water (= 103·2).

SIDEROSE. A name of native ferrous carbonate.

SIDEROSILICITE. A mineral forming, together with trinacrite, a brown mass on the tufa of Tonnara, at Cape Passaro, the southernmost point of Sicily. It has not been isolated, but, by calculation from the composition of the mixture, it appears to contain 34·04 per cent. silica, 7·48 alumina, 48·54 ferric oxide, and 10·13 water. (Waltershausen, *Vulk, Gesteine*, p. 234.)

SIDEROTANTALITE. See TANTALITE.

SIDEROTYPE. A method of producing sun-pictures by means of ammonio-ferric citrate. Paper impregnated with this salt is exposed to light in the camera, and the picture is developed with a neutral solution of gold or, better, of silver. (Herschel, Phil. Mag. [3] xxi. 225.)

SIBERITE. Red tourmalin.

SIEGENITE. Syn. with NICKEL-LINNÆITE (iv. 44).

SIENITE. Syn. with SYENITE.

SILEX. The old name of SILICA.

SILICA. SiO^2. *Oxide of Silicium, Silicic Oxide, Silicic Anhydride, Anhydrous Silicic Acid* (*Silice, Acide silicique. Kieselerde, Kieselsäure*).—This compound occurs abundantly, and pure or nearly pure, in quartz, flint, chalcedony, hornstone, jasper, opal, &c.; crystalline in quartz and its varieties; amorphous in opal (iv. 204; v. 1). It is the chief constituent of all sandstones, and enters largely into the composition of felspar and a great number of other minerals.

Silica is produced artificially:

1. By burning silicium in the air or in oxygen gas.
2. By the action of water on gaseous fluoride of silicium:

$$SiF^4 + 2H^2O = SiO^2 + 4HF.$$

The silica is thereby precipitated as a gelatinous hydrate, which, when dried and ignited, leaves pure anhydrous silica in the form of an extremely fine white powder.

3. By the decomposition of alkaline silicates.—Pure pulverulent silica may be prepared by fusing ground flint with about three times its weight of an alkaline carbonate, and decomposing the resulting compound with hydrochloric acid. A good mode of operating is to fuse a mixture of the carbonates of potassium and sodium in equivalent proportions at a red heat, and add ground flint or quartz to the melted mass by small quantities at a time, each addition causing a brisk effervescence, due to the escape of carbonic anhydride. The mixture is then heated strongly for some minutes, and, after cooling, treated with dilute hydrochloric acid, which decomposes it completely. On evaporating the liquid, the silica is separated as a gelatinous hydrate, which, on continuing the heat, is ultimately converted into a white earthy powder, consisting of anhydrous silica. It must then be digested with oil of vitriol, to remove any traces of

titanic oxide that may be present, freed from the strong acid by decantation, and lastly washed, dried, and ignited: it is then quite pure.

Silica may likewise be obtained nearly pure by heating quartz or flint to redness and quenching it in water; it is thus rendered friable, and may easily be reduced to a fine powder.

Properties.—The physical characters of natural silica, both crystalline and amorphous, have been described under Opal and Quartz. The crystalline variety has the higher specific gravity, ranging from 2·5 to 2·8, that of amorphous silica being between 1·9 and 2·3. Quartz is also very hard, being capable of scratching glass; the hardness of opal is somewhat less.

Silica, whether natural or artificial, crystallised or amorphous, requires a very high temperature to fuse it. In the flame of the oxyhydrogen blowpipe, or of a spirit-lamp fed with oxygen gas, it melts to a transparent glass, which may be drawn out into long threads. It is not volatile when heated alone, but it is said to volatilise when very strongly heated in a current of steam (*Gmelin's Handbook*, iii. 355), and has been found in the throats of iron-smelting furnaces, in concretionary nodules having a radio-fibrous structure (Scheerer; H. Rose, Jahresb. 1859, p. 147). Before the blowpipe silica decomposes carbonate of sodium with effervescence, and melts to a glass which is perfectly transparent, provided the silica is pure. In microcosmic salt it is almost insoluble.

Silica is decomposed by potassium at a red heat, yielding silicide and silicate of potassium; by carbon, in presence of iron, copper, or silver, at a white heat, into carbonic oxide and silicide of iron, copper, or silver; by hydrofluoric acid into water and fluoride of silicon.

Native silica, whether crystalline or amorphous, is insoluble in water and in all acids except hydrofluoric acid; so likewise is finely divided artificial silica after ignition; and even in the gelatinous state, as separated by acids from alkaline silicates, it is almost insoluble in water and in acids. The gelatinous hydrate obtained in the decomposition of silicic fluoride by water, dissolves, however, in a considerable quantity of water (Berzelius). In alkalis silica dissolves with greater facility. Freshly precipitated unignited silica dissolves in aqueous caustic potash or soda at ordinary temperatures, and even after strong ignition it dissolves slowly but completely in a cold, and rapidly in a boiling solution of caustic alkali. The different kinds of opal which, like precipitated silica, are amorphous, behave in the same manner with alkalis. Hyalite dissolves more slowly than the other varieties in cold aqueous alkalis. Quartz, even in a state of minute division, is perfectly insoluble in a cold solution, and dissolves but slowly in a boiling solution, of caustic alkali; but under pressure it dissolves more easily, forming a solution of an alkaline silicate.

Finely divided amorphous silica and gelatinous silica dissolve also to a slight extent in alkaline carbonates, which are only partially decomposed thereby, and deposit the silica again on cooling in the form of an opalescent jelly, containing a small quantity of the alkali. It appears to be owing to the solubility of silica in alkaline carbonates, that almost all spring and river waters contain minute quantities of silica in solution. When the action of the alkaline liquid is aided by a high temperature, as in the Geysers of Iceland, very large quantities of silica are dissolved; and as the liquid cools, the silica is deposited on the sides of the basin, or as petrifications on bodies contained therein.

Hydrates of Silica.—Silica is precipitated from solutions of alkaline silicates by acids, in the form of a gelatinous hydrate, which, as already observed, is nearly insoluble in water and in acids. If, however, a dilute solution of an alkaline silicate be poured into a considerable excess of hydrochloric acid, the whole of the silica is retained in solution, but may be precipitated by gradually neutralising the acid with an alkali.

From the solution of alkaline silicate in excess of hydrochloric acid, Graham (Phil. Trans. 1861, p. 204) obtains a pure solution of hydrate of silica by subjecting the liquid to dialysis in a hoop-dialyser of parchment-paper (iii. 716). If a stratum of liquid $\frac{4}{10}$ of an inch in depth be subjected for four or five days to dialysis, changing the water in the outer vessel at intervals of 24 hours, the hydrochloric acid and the soluble chlorides diffuse so completely into the water, that the liquid in the dialyser no longer gives a precipitate with nitrate of silver.

A solution may be thus obtained, containing 5 per cent. of silica, and by boiling it down in a flask, it may be concentrated till the quantity of silica reaches 14 per cent.; in open vessels it is apt to gelatinise on the edge, and the whole then solidifies. The solution is tasteless, limpid, and colourless, with a feeble acid reaction, rather greater than that of carbonic acid; 100 pts. of silica require 1·85 pts. of potash (K^2O) to neutralise their acid reaction upon litmus. The solution is not easily preserved for many days, as it becomes converted into a solid transparent jelly, which shrinks and gives up water even in closed vessels. The coagulation is retarded by hydrochloric acid, and by small quantities of caustic potash or soda. Sulphuric, nitric, and acetic acids are without action on the solution, but it is slowly coagulated by a few bubbles of carbonic acid. Its coagulation is also effected in a few minutes by the addition of $\frac{1}{1000}$ part of any alkaline or earthy carbonate in solution, but not by caustic ammonia, or by its salts, either neutral or acid. Alcohol, sugar, gum, and caramel are without action on it, but solutions of gelatin, soluble alumina, and soluble ferric oxide (iii. 717) immediately cause a gelatinous precipitate: when solution of silica is gradually added to solution of gelatin in excess, the precipitate formed consists of 100 pts. silica and 92 pts. gelatin.

The solution, evaporated at 15·5° in a vacuum, leaves the silica in the form of a transparent glassy, very lustrous hydrate, containing, after two days' exposure over oil of vitriol, 21·99 per cent. water, which agrees nearly with the formula $H^2O.SiO^2$ or H^2SiO^3.

Other hydrates of silica have also been obtained, but it is difficult to fix their composition exactly, as silica easily loses a portion of its water, even at low temperatures, and is moreover very hygroscopic. Ebelmen (Ann. Ch. Phys. [3] xvi. 129), by the action of moist air upon silicic ether, obtained a transparent glassy hydrate, containing $3H^2O\ 2SiO^2$. Doveri (*ibid.* xxi. 40), by drying ordinary gelatinous silica in vacuo over oil of vitriol at ordinary temperatures, obtained a hydrate, which had the composition $2H^2O.3SiO^2$, and gave off half its water at 100°. Fuchs (Ann. Ch. Pharm. lxxxii. 119), by drying gelatinous silica (prepared by passing gaseous fluoride of silicium into water) over oil of vitriol for 30 days, obtained the hydrate $H^2O.3SiO^2$, containing 9·1 to 9·6 per cent. water; and by drying it at 100° for 18 days he obtained another hydrate containing 6·6 to 6·7 per cent. water, agreeing with the formula $H^2O.4SiO^2$.

A very white and light hydrate of silica occurs abundantly in certain beds situated at the base of the chalk-formation, between the upper greensand and the gault. The proportion of hydrated silica in these deposits varies greatly, ranging from 5 to as much as 72 per cent., and being most abundant in the upper portion of the deposit.

SILICATES, ALCOHOLIC. See SILICIC ETHERS.

SILICATES, METALLIC. These salts occur abundantly as natural minerals, constituting in fact the greater part of the earth's crust. Many silicates may also be produced artificially, by fusing silica with metallic oxides, or with carbonates, sulphates, and other salts containing volatile acids. Some of the products thus obtained are exactly similar, in crystalline form and other characters, to natural minerals of the same composition. Some silicates, as those of potassium and sodium, are exclusively artificial products. (On the artificial formation of silicates, see Lefort, J. Pharm. [3], xxxix. 110; Jahresb. 1861, p. 205. H. Deville, Compt. rend. liv. 324; Jahresb. 1862, p. 138. B. v. Ammon, Jahresb. 1862, p. 138).

The silicates exhibit great diversity of composition. Those which occur as natural minerals contain proportions of metallic oxide and silica, included between the following limits:

α. For silicates containing only monatomic and diatomic metals $\left.\begin{matrix}4M^2O\\ \text{or } 4M''O\end{matrix}\right\}SiO^2$ and $\left.\begin{matrix}M^2O\\ \text{or } M''O\end{matrix}\right\}2SiO^2$.

β. For silicates containing triatomic metals: $2R^2O^3.SiO^2$, and $R^2O^3.6SiO^2$.

Some of the artificial silicates contain larger proportions of acid; thus by fusing silica with the carbonates of potassium and sodium in the proper proportions, tetrasilicates, $K^2O.4SiO^2$ and $Na^2O.4SiO^2$, are produced; potash is also said to form an octosilicate, $K^2O.8SiO^2$.

The following table exhibits the composition of the several groups of natural silicates, together with the ratios of the quantities of oxygen contained in the base and acid (SiO^2) in each case. The symbol M in the table denotes a monatomic metal: the substitution of equivalent quantities of diatomic and triatomic metals is easily made, the formula in the latter case sometimes requiring to be multiplied by three:—

Composition of Natural Silicates.

Name of Group.*	Oxygen-ratio $M^2O : SiO^2$	Formula.†	Examples.
Hexbasic	$1 : \frac{1}{3}$	$6M^2O.SiO^2 = M^{12}SiO^8$	Collyrite $2Al^2O^3.SiO^2 = \overset{\prime\prime\prime}{\bar{Al}}{}^4SiO^8$
Tetrabasic: tetartosilicates	$1 : \frac{1}{2}$	$4M^2O.SiO^2 = M^8SiO^6$	Staurolite (St. Gothard) $(\frac{5}{8}Al^{\prime\prime\prime}.\frac{1}{8}Fe^{\prime\prime\prime})^8Si^3O^6$
$\frac{2}{7}$-silicates	$1 : \frac{4}{7}$	$7M^2O.2SiO^2 = M^{14}Si^2O^{11}$	Margarite $\left.\begin{matrix}Ca^{\prime\prime}; Mg^{\prime\prime}; K^2; Na^2\\(Al^{\prime\prime\prime}; Fe^{\prime\prime\prime})^4\end{matrix}\right\} Si^2O^{11} + aq.$
$\frac{3}{10}$-silicates	$1 : \frac{3}{5}$	$10M^2O.3SiO^2 = M^{20}Si^3O^{16}$	Thuringite $(\overset{\prime\prime}{Fe}{}^4\overset{\prime\prime\prime}{\bar{Al}}{}^4)Si^3O^{16}$
Tribasic: tritosilicates	$1 : \frac{2}{3}$	$3M^2O.SiO^2 = M^6SiO^5$	Cyanite; Andalusite $\overset{\prime\prime\prime}{\bar{Al}}{}^2SiO^5$
$\frac{3}{8}$-silicates	$1 : \frac{3}{4}$	$8M^2O.3SiO^2 = M^{16}Si^3O^{14}$	Chondrodite $\overset{\prime\prime}{Mg}{}^8Si^3O^{14}$
$\frac{2}{5}$-silicates	$1 : \frac{4}{5}$	$5M^2O.2SiO^2 = M^{10}Si^2O^9$	Euclase $(\overset{\prime\prime}{Gl}{}^2\overset{\prime\prime\prime}{\bar{Al}}{}^2)Si^2O^9 + aq.$
Dibasic: hemisilicates, or Orthosilicates	$1 : 1$	$2M^2O.SiO^2 = M^4SiO^4$	Fayalite $\overset{\prime\prime}{Fe}{}^2SiO^4$ Olivine $(Mg^{\prime\prime}Fe^{\prime\prime})SiO^4$ Garnet $(\overset{\prime\prime}{Ca}{}^3\overset{\prime\prime\prime}{\bar{Al}}{}^2)Si^3O^{12}$
$\frac{9}{16}$-silicates	$1 : 1\frac{1}{8}$	$16M^2O.9SiO^2 = M^{32}Si^9O^{34}$	Nepheline $(Na^8\overset{\prime\prime\prime}{\bar{Al}}{}^8)Si^9O^{34}$
$\frac{3}{5}$-silicates	$1 : 1\frac{1}{5}$	$5M^2O.3SiO = M^{10}Si^3O^{11}$	Prehnite $(\overset{\prime\prime}{Ca}{}^2\overset{\prime\prime\prime}{\bar{Al}}{}^2)Si^3O^{11}$
$\frac{5}{8}$-silicates	$1 : 1\frac{1}{4}$	$8M^2O.5SiO^2 = M^{16}Si^5O^{18}$	Barsowite $(\overset{\prime\prime}{Ca}{}^2\overset{\prime\prime\prime}{\bar{Al}}{}^4)Si^5O^{18}$ Dichroïte $\left.\begin{matrix}\overset{\prime\prime}{Mg}{}^2\\(Al^{\prime\prime\prime}; Fe^{\prime\prime\prime})^4\end{matrix}\right\} Si^5O^{18}$
$\frac{2}{3}$-silicates	$1 : 1\frac{1}{3}$	$3M^2O.2SiO^2 = M^6Si^2O^7$	Serpentine $\overset{\prime\prime}{Mg}{}^3Si^2O^7 + 2$ aq. Degeroïte $\overset{\prime\prime}{Fe}{}^2Si^2O^7$
$\frac{3}{4}$-silicates	$1 : 1\frac{1}{2}$	$4M^2O.3SiO^2 = M^8Si^3O^{10}$	Scolecite $(Ca^{\prime\prime}\overset{\prime\prime\prime}{\bar{Al}}{}^2)Si^3O^{10}$
Monosilicates, or Metasilicates	$1 : 2$	$M^2O^3.SiO^2 = M^2SiO^3$	Wollastonite $Ca^{\prime\prime}SiO^3$ Diopside $(Ca; Mg)^{\prime\prime}SiO^3$
$\frac{9}{8}$-silicates	$1 : 2\frac{1}{4}$	$8M^2O.9SiO^2 = M^{16}Si^9O^{26}$	Oligoclase $\left.\begin{matrix}(Ca^{\prime\prime}; Mg^{\prime\prime}; K^2; Na^2)^2\\\overset{\prime\prime\prime}{\bar{Al}}{}^4\end{matrix}\right\} Si^9O^{26}$
$\frac{5}{4}$-silicates	$1 : 2\frac{1}{2}$	$4M^2O.5SiO^2 = M^8Si^5O^{14}$	Talc $\overset{\prime\prime}{Mg}{}^4Si^5O^{14} + \frac{4}{3}$ aq.
$\frac{6}{5}$-silicates	$1 : 2\frac{2}{5}$	$5M^2O.6SiO^2 = M^{10}Si^6O^{17}$	Pectolite $(Na^2\overset{\prime\prime}{Ca}{}^4)Si^6O^{17}$
Sesquisilicates	$1 : 3$	$2M^2O.3SiO^2 = M^4Si^3O^8$	Orthoclase $(KAl^{\prime\prime\prime})Si^3O^8$ Stilbite $(Ca^{\prime\prime}\overset{\prime\prime\prime}{\bar{Al}}{}^2)Si^6O^{16} + 5$ aq.
Disilicates, or Bisilicates	$1 : 4$	$M^2O.2SiO^2 = M^2Si^2O^5$	Okenite $Ca^{\prime\prime}Si^2O^5 + 2$ aq. Beaumontite $(Ca^{\prime\prime}\overset{\prime\prime\prime}{\bar{Al}}{}^2)Si^8O^{20} + 6$ aq. Petalite $[(Li; Na)^6\overset{\prime\prime\prime}{\bar{Al}}{}^8]Si^{30}O^{75}$

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* Silicates are sometimes distinguished by names which express directly the oxygen-ratio in the base and acid, the ratio 1 : 1 giving *Singulosilicates*, 1 : 2 *Disilicates*, 1 : 3 *Trisilicates*, 1 : 4 *Quadrosilicates*, &c.

† To convert the formulæ in this table into the older formulæ in which silica is regarded as a trioxide, $\mathfrak{S}iO^3$, multiply the entire formula by 3, correct the silica term by the equation $1SiO^2 = \frac{2}{3}\mathfrak{S}iO^3$, and reduce the whole to its lowest terms: *e.g.*—$2M^2O.SiO^2 = 3M^2O.\mathfrak{S}iO^3$; $M^2O.SiO^2 = 3M^2O.2\mathfrak{S}iO^3$; $2M^2O.3SiO^2 = M^2O.\mathfrak{S}iO^3$. Conversely, to change formulæ containing $\mathfrak{S}iO^3$ into those containing SiO^2, divide by 3, and correct for $1\mathfrak{S}iO^3 = \frac{3}{2}SiO^2$.

The dibasic silicates in which the oxygen-ratio is 1 : 1, are regarded as normal or orthosilicates, and from these the mono- or metasilicates may be derived by abstraction of 1 at M^2O. These two groups, together with the sesquisilicates (2 : 3), include the most numerous and important of the natural silicates. Many of the ordinary varieties of glass may be approximately represented by mixtures of silicates of potassium, sodium, calcium, &c. belonging to the group of disilicates.

Hydrated silicates may be referred to one or other of the preceding groups, according as more or less of their water is regarded as basic: thus dioptase may be formulated either as a hemisilicate, $Cu''H^2SiO^4$, or as a hydrated monosilicate, $Cu''SiO^3.H^2O$. In like manner okenite, represented in the above table as a hydrated disilicate, $Ca''Si^2O^5.H^2O$, may also be formulated as a monosilicate, $(Ca''H^2)Si^2O^6$.

Most silicates are fusible, and their fusibility is increased by mixture with each other: those which contain readily fusible oxides melt at the lowest temperatures, and in general the most easily fusible silicates are those which contain the largest proportion of base.

All silicates are insoluble in water, excepting the silicates of the alkali-metals, which dissolve with greater facility in proportion as they contain a larger quantity of base.

Some silicates are entirely decomposed when pulverised and treated with hydrochloric or nitric acid, the bases being dissolved and the silica being sometimes separated in a pulverulent or gelatinous form, sometimes dissolved either wholly or in part, the solution then yielding a jelly on evaporation. Sulphuric acid diluted with a small quantity of water, likewise decomposes the greater number of silicates when reduced to powder. Some silicates, on the contrary, resist the action of all acids except the hydrofluoric. In general silicates are more easily decomposed by acids; the stronger the bases contained in them, the less the silica predominates, and the larger the proportion of water present: on this account many silicates containing water—zeolites for example—lose their solubility in hydrochloric acid after ignition. All silicates without exception become soluble in dilute hydrochloric or nitric acid: after fusion with from 3 to 5 times their weight of hydrate or carbonate of potassium or sodium, or with carbonate of barium, strontium, or calcium, or with oxide of lead; they become completely disintegrated, and the solution yields on evaporation, first a jelly and then a dry residue, of which the part which is insoluble in hot hydrochloric acid exhibits the characters of silica. Andalusite, cyanite, staurolite, and zircon, require a full white heat to disintegrate them perfectly with an alkaline carbonate, and are more readily acted on by hydrate of potassium. From the native silicates, whether simple or double, which contain potash, soda, or lithia, the alkali may be separated by igniting them with lime, and treating the ignited mass with water. With many, however, as in the case of nepheline, leucite, natrolite, analcime, and chabasite, it is sufficient even to ignite them by themselves, and afterwards boil them in a finely divided state, with milk of lime, or to digest them with it for a longer time in the cold. Clays treated in this manner likewise give up to water the small proportion of potash or soda which they contain; and if they happen to be rich in carbonate of calcium, they merely require to be digested in water after ignition. Volcanic rocks, such as phonolitic lava, give up the potash or soda they contain by digestion with milk of lime, even without previous ignition.

Silicates heated with *fluor-spar* and *oil of vitriol* in a platinum vessel, evolve gaseous fluoride of silicon, which, when the vessel is covered with moistened felt, deposits upon it white flakes of hydrate of silica.—The same gas is evolved, with effervescence, when a silicate in the state of powder is immersed in a strong solution of hydrofluoric acid. *Microcosmic salt* in the blowpipe-flame withdraws the base from the silicates, and sets the silicic acid free. The product is a translucent, blistered mass. When a small quantity only of the microcosmic salt is used, the mass diffuses itself through the silicious crust; when the quantity of flux is larger, the silica floats in the fused bead. When only a small quantity of silica is present, the glass is clear while fused, but becomes turbid on cooling; with still less silica however it remains transparent (Berzelius).—Silicates heated with *carbonate of sodium* before the blowpipe, expel the carbonic acid with effervescence. The silicates of the alkali-metals and of most of the heavy metals yield a transparent glass; those of the earth-metals yield sometimes a clear and sometimes a turbid glass, according to the proportions of silica and of base. If the silica contains at least twice as much oxygen as the earthy base, the latter is dissolved in the glass by the agency of the silica, and the glass remains clear. If the compound contains less silica, it yields a clear glass with a comparatively small proportion of sodic carbonate; but with a larger proportion, it forms a turbid glass, and with a still larger quantity an infusible slag; for the greater the amount of soda, the greater also is the quantity of the earthy base which is separated by its action. (Berzelius.)

Quantitative Analysis of Silicates. Estimation of Silica.

For the analysis of silicates which are completely decomposed by acids, it is sufficient to boil the finely pulverised mineral with strong hydrochloric acid as long as anything continues to dissolve, then evaporate to dryness, and boil the residue with water containing hydrochloric acid: this will dissolve everything excepting the silica, which may then be washed, dried, ignited, and weighed. The liquid filtered from the silica contains the bases of the mineral, which may be separated by the usual methods.

To ensure the complete separation of the silica, it must be perfectly dried before boiling it with the acidulated water. Now to ensure this complete dryness, it is necessary to heat the silica somewhat above the temperature of the water-bath, the desiccation being completed over a sand-bath or a lamp. In doing this it sometimes happens that too much heat is applied, and in that case a portion of the bases, especially alumina and ferric oxide, may also be rendered insoluble in the dilute acid. To obviate this source of error, the dried residue must be moistened all over with strong hydrochloric acid, then left to stand for half an hour, and afterwards boiled with water. Everything will then dissolve excepting the silica.

Silicates which, like felspar, resist the action of hydrochloric acid, are decomposed by fusion with an *alkaline carbonate*. The mineral, very finely powdered, is mixed in a platinum crucible with three or four times its weight of dry carbonate of sodium; or better with a mixture of the carbonates of potassium and sodium in equivalent proportions, which fuses more readily; the platinum crucible is heated to bright redness for about twenty minutes in a gas furnace (ii. 784, 789), or placed within an earthen crucible half filled with carbonate of magnesium, and heated in an ordinary coke furnace; the fused mass, when cold, is removed from the crucible by digestion in dilute hydrochloric acid with the aid of heat; the whole is evaporated to dryness; the silica separated; and the bases are determined as above.

Some native silicates, as zircon, cyanite, cymophane, &c., are decomposed with difficulty by fusion with alkaline carbonates, requiring a very strong heat continued for a long time. In these cases the decomposition may be facilitated by the addition of a fragment of potassic or sodic hydrate, which however, to avoid injuring the crucible, must be introduced into a cavity made in the middle of the mixture of silicate and carbonate, after it has been heated for a short time, not sufficiently to melt it, and solidly pressed down into the crucible.

By these processes, not only the silica, but all the bases of a silicate may be determined, excepting the alkalis. To determine these, the mineral, reduced to an almost impalpable powder, is very intimately mixed with five times its weight of pure *carbonate of calcium*, and the mixture exposed in a platinum crucible, protected as above, to the strongest heat of an air-furnace or a blast gas-furnace (ii. 785) for about half an hour. The mass, which is not fused, but sintered together, is then digested in dilute hydrochloric acid; the silica separated as before; the greater part of the lime and likewise the bases of the silicate precipitated by carbonate of ammonium and free ammonia; the filtrate evaporated to dryness, and the ammoniacal salts expelled by ignition; the residue redissolved in water; the remainder of the lime precipitated by oxalate of ammonium; and the ammoniacal salts again expelled by evaporation and ignition. The residue then contains nothing but the chlorides of the alkali-metals and magnesium, if that substance was contained in the mineral. *Carbonate of barium* may also be used instead of carbonate of calcium, and the excess of barium removed by sulphuric acid.

Another method of obtaining the alkalis in a silicate, is to decompose it with *hydrofluoric acid* aided by a gentle heat. The acid must be added by small portions to the finely pulverised mineral contained in a platinum dish, till the action ceases and the whole is reduced to a pasty mass. This mass is then heated with strong sulphuric acid, which expels fluoride of silicon and hydrofluoric acid; the residue is heated to low redness to expel the excess of sulphuric acid; the dry mass, when cold, is moistened with strong hydrochloric acid, and, after standing for about half an hour, digested with water. The whole then dissolves, provided the decomposition by the hydrofluoric acid has been complete. The solution contains the alkalis and the other bases in the state of sulphates.

Fluoride of ammonium may also be used instead of hydrofluoric acid: it acts more energetically, and decomposes certain silicates which offer considerable resistance to the action of hydrofluoric acid. The finely pulverised mineral is mixed in a platinum dish with seven times its weight of the ammonium-fluoride, and made up into a paste with a small quantity of water. The mixture is gently heated for some time in order to dry it completely, then to dull redness till it no longer gives off any vapour. The dry mass is treated with sulphuric acid, the excess of that acid expelled by evaporation, and the residue digested with water. The whole then dissolves if the decomposition has been complete; in the contrary case a residue is left, which must be again treated with fluoride of ammonium. Nearly all silicates yield to this treatment; zircon, however, is not completely decomposed by it, and must be treated with carbonate and hydrate of sodium as above described. (H. Rose, *Traité de Chimie analytique*, ii. 867.)

Estimation of Water and other volatile substances in Silicates.—The water in most hydrated silicates is easily estimated by heating the pulverised mineral to redness in a platinum crucible, the whole of the water being then driven off without any further alteration of the silicate. Some silicates, however, euclase and idocrase for example, retain their water with great force, parting with it only at very high temperatures. In such cases it is best to expose the mineral to an intense heat in a current of pure and dry air. Idocrase gives up its water only when heated nearly to its melting-point, and at the same time evolves a small quantity of carbonic acid, sufficient to produce a considerable cloud in baryta-water, but not large enough for quantitative estimation. Some silicates contain small quantities of organic matter as well as water, and when strongly heated in a current of hydrogen, give off water containing empyreumatic products and ammonia: this is especially the case with pitchstone. The quantity of carbon may be determined by ignition with oxide of copper, as in organic analysis, and the amount of hydrogen at the same time, if the mineral does not also contain water ready formed; but if water is also present, and is given off only at the same temperature as the organic matter, the determination becomes very difficult. The emerald contains water and likewise a small quantity of organic matter, to which its colour is due.

In some silicates there are other constituents to be estimated besides water, silica, and metallic bases. Thus datholite and botryolite contain boric acid; tourmaline contains boric acid and fluorine; sodalite and ittnerite contain chlorine; cancrinite contains carbonic acid; haüyne and ultramarine contain chlorine and sulphur; many silicates contain fluorine and phosphoric acid; titanic acid also is of frequent occurrence in silicates.

1. *Boric acid.*—The methods of analysing borosilicates have been already given under Boron (i. 631).

2. *Chlorine.*—Most silicates containing chlorine are easily decomposed by acids. To analyse them they are treated with cold nitric acid of specific gravity 1·2, which either dissolves them completely or separates a portion of the silica in the gelatinous form; in the latter case more water must be added, and the liquid left at rest till the separated silica has settled down. The clear solution is then treated with nitrate of silver, the precipitated chloride of silver is left to settle down in a cool place, then collected on a filter, and treated in the usual way (i. 904). The excess of silver is precipitated by hydrochloric acid, the filtrate evaporated to dryness to separate the silica, and the analysis completed in the same way as for other silicates. Pyrosmalite, which contains chlorine, is not easily decomposed by acids: its decomposition may however be effected by digesting it for several days with dilute nitric acid, at a moderate heat, the flask being corked to prevent escape of chlorine; or, better perhaps, by fusion with an alkaline carbonate. (H. Rose.)

3. *Fluorine.*—A great number of silicates contain fluorine, though often only in small quantity. Such silicates which, for the most part, are not decomposed, or only incompletely decomposed by acids, are analysed by fusing them with four times their weight of alkaline carbonate, and boiling the fused mass with water. The whole of the fluorine then dissolves in the form of alkaline fluoride, together with a certain portion of the silica and alumina in the mineral. The insoluble matter is collected on a filter and washed, first with pure water, then with water containing carbonate of ammonium. To separate the silica dissolved in the alkaline filtrate, the liquid is mixed with an alkaline solution of zinc-carbonate, which is added as long as a precipitate continues to form; then evaporated to dryness, and the dried mass treated with water, which leaves the whole of the silica undissolved, together with oxide of zinc. The insoluble residue is then to be treated with nitric acid, the silica separated by evaporation to dryness, &c., and weighed. The liquid filtered from the silicate of zinc contains the whole of the fluorine, as fluoride of sodium. The fluorine is precipitated from it by chloride of calcium, and estimated as fluoride of calcium (ii. 674).—The insoluble residue left on treating the original fused mass with water, contains the greater part of the silica, together with the bases. It is treated with hydrochloric acid, the silica separated, and the bases determined in the usual way, the silica thus obtained being of course added to the quantity precipitated by the zinc-solution. (H. Rose, *Traité de Chimie analytique*, ii. 890.)

4. *Phosphoric acid.*—When silicates containing phosphates are decomposed either by acids, or fusion with alkaline carbonates and subsequent treatment with hydrochloric acid, the whole of the phosphoric acid is found in the acid liquor, and may be separated from the bases and estimated by the methods already given (iv. 546).

When phosphoric acid and fluorine occur together in a silicate which is easily decomposible by acids, and contains no bases except the alkalis, the mineral is decomposed by nitric acid, the liquid is saturated with ammonia, without previous separation of the silica, an ammoniacal solution of zinc-carbonate is added, and the whole is evaporated to dryness over the water-bath. The dried mass is then treated with water, which dissolves the alkaline fluoride and nitrate, leaving a residue of phosphate and silicate of zinc, together with excess of zinc-oxide. The fluorine, silica, and phosphoric acid are then determined as above described.

If, on the other hand, the silicate contains alkaline earths, and especially lime, then, whether it is decomposible by acids or not, it must first be fused with four times its weight of a mixture of potassic and sodic carbonates. The fused mass is treated with water, and after complete disintegration, the liquor is filtered. The filtrate contains the whole of the fluorine and part of the phosphoric acid and silica in the form of alkaline salts, while the residue is composed of alkaline silicate, together with calcic silicate and phosphate, calcic phosphate never being completely decomposed by fusion with alkaline carbonate. The filtrate is treated with an ammoniacal solution of zinc-carbonate, and evaporated to dryness, and the residue is treated with water, which dissolves all the alkaline fluoride, leaving the silica and phosphoric acid as zinc-salts. The remainder of the analysis is the same as above.

5. *Sulphur and Sulphuric acid.*—Silicates containing sulphates are decomposed by hydrochloric acid, or by fusion with alkaline carbonate; and from the acid solution obtained, in the former case directly, in the latter by treating the fused mass with hydrochloric acid, the sulphuric acid is precipitated by chloride of barium.

When sulphur is present in a silicate in combination with a metal, it may be oxidised to sulphuric acid by the action of fuming nitric acid, or of hydrochloric acid and chlorate of potassium, or by fusion with a mixture of alkaline carbonate and nitrate. When the sulphur is present, partly as sulphate, partly as sulphide, the quantity existing in the latter form may sometimes be determined by heating the pulverised mineral with hydrochloric acid, passing the sulphydric acid thereby evolved into a solution of copper, collecting the precipitated sulphide of copper, and treating it as described under COPPER (ii. 57). The liquid remaining in the flask is then filtered to separate the silica, and the sulphur originally existing in the mineral as sulphuric acid is determined by precipitation with a barium-salt.

6. *Tantalic and Niobic acids.*—In silicates containing these acids (which, however, are of very rare occurrence), the quantity of silicon may be estimated by treating the compound with hydrofluoric acid, then adding sulphuric acid, and heating till the whole excess of the latter is expelled. The quantity of silica may then be estimated by loss. This method however is not very exact, because small quantities of tantalum and niobium are liable to be also driven off as fluorides. A better method is to fuse the mineral in a silver crucible with three times its weight of sodium-hydrate, and treat the fused mass with water, which dissolves all the silicon as sodic silicate, leaving tantalate or niobate of sodium undissolved. (H. Rose.)

7. *Titanic acid.*—The best method of treating silico-titanates is to heat them with fluoride of ammonium, and afterwards with sulphuric acid, in the manner already described (p. 245). The whole of the silicon is then expelled as gaseous fluoride, and a residue is obtained completely soluble in water, containing the bases as sulphates, together with the titanic acid, which must be separated and estimated by processes to be described hereafter (H. Rose). See TITANIUM.

Silicates containing only Monatomic and Diatomic Metals: Silicates of Protoxides.

Silicates of the Alkali-metals.—*Silicate of Ammonium* is not known in the solid state. Aqueous ammonia dissolves a large quantity of freshly precipitated silica. Carbonate of ammonia dissolves it but sparingly.

The silicates of potassium and sodium resemble each other so closely that it will be convenient to describe them together. They contain various proportions of acid and base, and are all more or less soluble in water, those which contain the largest proportions of alkali dissolving the most easily.

The alkaline silicates are prepared either by fusing silica with the hydrates, carbonates, nitrates, or other salts of the alkali-metals containing volatile acids, or by boiling flint, sand, &c., with strong solutions of the caustic alkalis under pressure. When 1 part of silica is fused with 2¼ pts. carbonate of potassium, or with 1¾ pt. anhydrous carbonate of sodium, a transparent glass is produced consisting of an alkaline monosilicate, $K^2O.SiO^2$, or $Na^2O.SiO^2$. These salts deliquesce in the air and dissolve readily in water, forming an alkaline solution called *liquor silicum.* When a strong solution of this monosilicate is treated with hydrochloric or nitric acid, the greater part of the silica is precipitated in gelatinous flocks, a certain quantity however always remaining dissolved: but if the solution of the silicate be largely diluted, and a quantity of hydrochloric acid added sufficient to give it a strong acid reaction, no precipitate is formed, but the whole of the silica remains dissolved.

Alkaline silicates containing a larger proportion of silica, but still with a sufficient quantity of alkali to make them completely soluble in water, are denominated "water-glass." These salts are prepared on the manufacturing scale, and applied to several purposes in the arts.

Fuchs of Munich, who first proposed them for economical use, adopts the following processes:—

1. To prepare potash water-glass, a mixture of 15 pts. pulverised quartz or sand, 10 pts. of well purified pearlash, and 1 pt. of powdered charcoal, is ignited for five or six hours at a temperature equal to that required to melt common glass. The proportions of silica and alkali used are about sufficient to form a tetrasilicate, $K^2O.4SiO^2$, allowing for impurities in the pearlash. The use of the charcoal is to facilitate the decomposition of the alkaline carbonate, and decompose any sulphuric acid that may be present. The fused mass is then left to cool, pulverised, and boiled with 5 times its weight of water in an iron pot for three or four hours, the water being renewed as it evaporates. After the whole is dissolved, the boiling is continued, so as to concentrate the solution to a specific gravity of 1·24 to 1·26. In this state it is sufficiently liquid to be used in many operations, but in some cases it requires to be diluted and in others to be evaporated to a syrupy consistence. If it contains any sulphide of potassium (arising from decomposition of the sulphate by the charcoal), a small quantity of oxide of copper or litharge must be added to convert it into hydrate, a certain excess of which renders the water-glass better adapted for many purposes. If, however, a perfectly saturated silicate is required, the saturation may be ensured by boiling the liquid with recently precipitated silica. The solution, purified as just described, is left to cool and clarify, the vessel being well closed to prevent access of air. The clear liquid is then decanted from the deposit (which makes a good manure), and stored in carboys; or it may be evaporated to a jelly and packed in tinned iron vessels.

Water-glass may be obtained in the solid state by mixing the concentrated solution with about one-fourth of its volume of rectified spirit; a gelatinous precipitate is thereby formed, which contracts strongly in a few days, and is deposited in a solid mass; and if the supernatant liquid (containing alkaline carbonates, chlorides, and sulphides) be decanted, and the deposit slightly washed and squeezed, the water-glass is obtained in the solid state, and consisting, according to Fuchs, of potassic tetrasilicate, $K^2O.4SiO^2$, perfectly soluble in water. According to Forchhammer, however, the alcohol, even in the act of precipitation, and still more during the subsequent washing, withdraws a portion of the alkali, until the residue consists of octosilicate, $K^2O.8SiO^2$, which is not completely soluble in water. According to Frémy (Jahresb. 1856, p. 353), the salt precipitated from a solution of potassic silicate by alcohol, has the composition $2K^2O.9SiO^2.aq.$; and the sodic silicate obtained in like manner is $2Na^2O.9SiO^2.20aq.$; according to Lefort (*ibid.* 1861, p. 205), both the salts thus precipitated have the composition $2M^2O.9SiO^2.aq.$

2. Soda water-glass is prepared in a similar manner, the proportions being 45lbs. of quartz, 23lbs. anhydrous carbonate of sodium, and 3lbs. of charcoal: this gives a product having nearly the composition $2Na^2O.5SiO^2$: it fuses more readily than the potash-glass. According to Buchner, soda water-glass may be prepared more economically by means of sodic sulphate, in the proportion of 100 pts. quartz, 60 pts. anhydrous sodic sulphate, and 15 to 20 pts. charcoal-dust.

By dissolving the product obtained by either of these processes in boiling water, and saturating it with recently precipitated silica, it may be converted into the tetrasilicate $Na^2O.4SiO^2$. Rectified spirit does not precipitate this compound so completely as the potash-glass, but merely converts it into a gelatinous mass: in solutions not completely saturated with silica, or slightly diluted, it forms a precipitate.

3. Double water-glass.—Potash and soda water-glass are miscible in all proportions. Normal double water-glass, containing equivalent quantities of potash and soda, may be obtained by fusing together 100 pts. of quartz and 121 pts. of sodio-potassic tartrate (Rochelle salt); or more cheaply by fusing a mixture of potassic and sodic nitrates in equivalent proportions with the corresponding quantity of quartz, or 100 pts. quartz, 28 pearlash, 22 anhydrous carbonate of sodium, and 6 powdered charcoal. This mixture fuses more readily than any of the preceding. A solution of double water-glass suitable for all practical applications, may likewise be prepared by mixing 3 measures of concentrated potash water-glass with 2 measures of concentrated soda water-glass.

Soluble silicates may also be obtained by boiling silica with solutions of caustic alkalis under pressure. The following process, patented in 1844 by Mr. Ransome of Ipswich, is essentially the same as that adopted by Kuhlmann of Lille:—100 lbs. of crystallised sodic carbonate, or 50 lbs. of pearlash, are dissolved in about 50 gallons of water, and the solution, after being rendered caustic by means of lime, is reduced to the bulk of 20 or 25 gallons by heat. This caustic ley is then introduced together with 100 lbs. of finely broken flints or other convenient silicious substance, into an iron boiler or digester, and the mixture is heated with frequent agitation for ten or twelve hours up to a pressure of about 60 lbs. to the square inch. When the mixture is sufficiently incorporated, it may be passed through a sieve to separate any undissolved matter.

The soluble silicates prepared by different manufacturers differ considerably in composition, seldom exhibiting that of a tetrasilicate. Of the following samples—*a* is soda water-glass from the manufactory of Seibel at Liesing; *b*, soda water-glass from Munich; *c*, potash water-glass from Kuhlmann's factory at Lille:—

	a.	*b.*	*c.*
Water . .	65·829	38·66	0·689
Silica . . .	22·258	44·64	63·000
Soda . . .	11·178	16·25	
Potash . .	. .	. .	34·400

a has, approximately, the composition of a disilicate; *b* that of a $\frac{5}{2}$-silicate; *c* that of a trisilicate.

Solid or fused water-glass, when pure, has the appearance of ordinary glass, and dissolves slowly, but completely, in boiling water; it becomes insoluble only when the proportion of silica is considerably increased. A concentrated solution, containing 28 per cent. of the alkaline silicate, is syrupy, somewhat turbid, and has a density of about 1·25. After evaporation at a high temperature, it becomes very tenacious, and may be drawn out into threads like melted glass. The solution is decomposed by *acids*, even by *carbonic acid*, the silica being separated in the gelatinous form. On exposure to the air, it becomes covered with a tough skin, which disappears when thrust beneath the liquid. During evaporating to dryness, it must be kept constantly boiling, to prevent access of carbonic acid. *Alkaline carbonates* and *chlorides*, especially sal-ammoniac, precipitate silica from the solution. *Baryta, strontia, lime, alumina*, and *oxide of lead* decompose it, removing the whole of the silica and a portion of the alkali in the form of a double silicate. Nearly all the soluble salts of the earth-metals and heavy metals likewise produce precipitates consisting of double silicates. *Phosphate of aluminium*, and *carbonate, phosphate*, and *sulphate of lead* triturated with a solution of water-glass, yield a tenacious mass, which acquires a stony hardness on exposure to the air. *Phosphate of calcium* is not decomposed by it.

Uses of Alkaline Silicates.—1. *As cements, and for hardening and preserving stone.*—The soluble silicates may be applied in various ways for imparting solidity to loose structures. This effect is due sometimes to a chemical action between the soluble silicate and the porous material, resulting in the formation of an insoluble silicate or double silicate—sometimes to the gradual decomposition of the alkaline silicate, resulting in great measure from the action of atmospheric carbonic acid, and the consequent deposition, between the particles of the porous material, of a mass of solid silica which binds them firmly together. Ransome, in 1845, patented a process for the application of a soluble silicate for combining small coal into blocks, and for preserving wood from fire and decay.

The action of soluble silicates on calcium-compounds is of particular importance. Water-glass sets rapidly when mixed with slaked lime, and slowly dries up to a hard mass, consisting of a double silicate of calcium and the alkali-metal, on which water has no action. A piece of chalk immersed in a solution of alkaline silicate, absorbs it, and on drying becomes nearly as hard as marble. Pulverised chalk or marble is also converted by water-glass into a hard compact mass; magnesian limestone is rendered still harder. This effect is due either to a combination of the alkaline silicate with the calcic carbonate, resulting in the formation of a compound similar to cancrinite (i. 734), or to a double decomposition resulting in the formation of calcic silicate, which then unites with the undecomposed portion of the carbonate; perhaps both these actions take place together. The silification of limestones is greatly facilitated by heating them with the silicious solution under pressure. Sulphate of calcium is acted upon by soluble silicates in the same manner as carbonate, but the resulting mass is less compact, in consequence, chiefly, of the greater rapidity of the action; a more dilute solution must therefore be used, so as to render the action slower.

These reactions of the soluble silicates have been successfully applied by Ransome, Kuhlmann, and others, to the production of artificial stone for building and ornamental purposes, and to the preservation of the stone of buildings actually constructed. To prepare artificial stone, a concentrated solution of water-glass is mixed with sand, broken flints, pieces of marble, &c., sometimes with addition of cream of lime; the whole being subjected to pressure in moulds, and afterwards dried in an oven. By this means stone of great hardness is obtained, and in some cases is capable of receiving a fine polish.

For hardening building stones, and protecting them from the action of acid vapours, Kuhlmann employs a solution of silicate of potassium. Silicate of sodium produces the same effect, but is said to give rise, after a while, to unsightly efflorescences. The solution is applied with a brush, or sprinkled on the walls of the building by means of large syringes with rose nozzles. The alkaline silicate being gradually decomposed by the action of the carbonic acid in the air, a coating of silica is deposited on the stone, which protects it from further atmospheric action. This process is said to have been successfully applied at the Louvre and the cathedral of Notre Dame in Paris, and to several buildings in other towns of France. In the moist climate of England, however, the application of alkaline silicates in this manner is attended with very uncertain results, the liquid coating being liable to be removed from the surface by rain, or even by the ordinary humidity of the air, before it has time to absorb sufficient carbonic acid to precipitate the silica in an insoluble form. This inconvenience may be obviated, and a much more compact silicious coating obtained, by washing the surface of the building first with a solution of alkaline silicate, and then with a solution of chloride of calcium, whereby an insoluble silicate of calcium is formed, possessing strongly cohesive properties and perfectly indestructible by atmospheric influences. This process was patented by Mr. Ransome in 1856, and is said to have been applied with good effect to many public buildings.

2. Another very important application of the alkaline silicates is to the art of *Mural Painting*. In ordinary fresco-painting, as is well known, the picture must be executed as soon as the coat of stucco is laid upon the walls, and finished before the stucco is dry; moreover, it cannot be afterwards retouched. Now by working on a surface of plaster prepared with a solution of water-glass, it is found that this inconvenience is completely obviated—that the painter can work at his leisure, and retouch the work as often as is found desirable. The first experiments on this subject were made by Fuchs, who designates this kind of mural painting by the name stereochromy.

Two methods of silicious painting have been proposed: one by Fuchs, in which the colours, ground up with water, are laid upon a prepared surface and afterwards fixed with a silicious solution; the other by Kuhlmann, in which the colours are ground up with the alkaline silicate. In Fuchs' method the wall is first coated with a layer of ordinary lime-mortar containing a rather large proportion of sand of medium fineness; and on this, when dry, is laid a second coating of lime-mortar prepared with rain or distilled water, and well-washed sand of greater fineness than that used for the first coating. This when dry is impregnated with a solution of double water-glass clarified with *liquor silicum* (p. 247), and diluted with an equal bulk of water. This solution is applied twice, allowing time for the first washing to dry.

In his latest essay on the subject, however, Fuchs recommends the preparation of the upper layer with water-glass cement—that is to say, water-glass intimately mixed with pounded marble or dolomite, or quartz-sand mixed with a little dry slaked lime—the water-glass being used in such quantity as to give the mass the consistence of ordinary mortar. The surface having been prepared, the painting is executed upon it with mineral colours ground up with pure water; and when it is finished, the colours are fixed by washing or sprinkling the surface with "fixing water-glass," consisting of a mixture of 4 or 5 measures of concentrated water-glass saturated with silica, and 1 measure of concentrated *liquor silicum* (monosilicate of sodium), the mixed liquid being diluted with half its bulk of water. Paintings thus executed are found to possess great durability and power of resisting destructive influences. Plates of earthenware, tiles, and lithographic stone impregnated with water-glass may also be used as grounds for silicious painting.

In Kuhlmann's method, the colours are ground up with the silicious solution, and consequently do not require so much preparation of the painting ground, or so much care in fixing. In painting upon stone, stucco, glass, &c., the colours, ground with water and kept in a pasty state, are immediately mixed with a silicious solution of 15° to 20° Bm., and applied exactly as in oil or distemper painting, except when the stone is very porous, in which case it is best to silicify the stone before applying the colours, to prevent too rapid desiccation. For glass and earthenware the silicious solution must be more concentrated. The silicious colours may also be used for painting on wood, provided it is not impregnated with resin.*

3. The alkaline silicates are also used to mix with soap, forming "silicated soaps,"

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* For a more detailed account of the preceding applications of soluble silicates, see a paper by Fuchs in *Kastner's Archives of Natural Philosophy*, v. 385—412; *Journal of the Society of Arts*, vii. 521—532; also a pamphlet by Kuhlmann, entitled *Silicatisation, ou applications des Silicates solubles au durcissement des pierres poreuses*, &c. Paris 1858; also Richardson and Watt's *Chemical Technology*, Part iv., pp. 69—104; v. pp. 348, 582.

which possess powerful detergent properties, and are extensively manufactured for the cleansing of woollens, &c. (See SOAP.)

4. A solution of silicate of sodium, as nearly neutral as possible, and having a specific gravity of 1·53, is now very generally used as a substitute for cowdung in preparing mordanted calico for dyeing.

The silicates of potassium and sodium unite with the silicates of calcium, lead, and other metals, forming the several varieties of glass. These double silicates are more fusible than either of their component simple silicates, and require a smaller quantity of silica to render them capable of resisting the action of water and acids. The ordinary varieties of glass contain 2, 3, or sometimes 4 atoms of silica in proportion to 1 atom of base; common bottle-glass, prepared with impure materials, also contains alumina and oxide of iron. Bohemian glass-tubing consists of potassio-calcic trisilicate, $\left\{\begin{matrix}2(K^2O.3SiO^2)\\3(Ca''O.3SiO^2)\end{matrix}\right.$; window-glass of sodio-calcic disilicate, $\left\{\begin{matrix}Na^2O.2SiO^2\\Ca''O.2SiO^2\end{matrix}\right.$; flint-glass of potassio-plumbic disilicate, $\left\{\begin{matrix}2(K^2O.2SiO^2)\\3(Pb''O.2SiO^2)\end{matrix}\right.$, &c. (See GLASS, ii. 840.)

The alkaline silicates do not occur alone as natural minerals; neither do they enter frequently into the composition of silicates containing only protoxides without alumina or ferric oxide: in fact, there are only two such minerals into which the alkali-metals can be said to enter in definite proportions—viz., apophyllite, which is a potassio-calcic silicate, and pectolite, which is a sodio-calcic silicate (iv. 362). Some varieties of augite and hornblende contain indeed small quantities of alkali, but its presence appears to be due to alteration, resulting from the action of alkaline waters. On the other hand, double silicates containing sesquioxides (alumina and ferric oxide) and alkalis are of frequent occurrence, and constitute important mineral species, the felspars and micas for example.

Silicates of Barium. One part of silica heated to whiteness forms, with 3 parts of baryta, a pale-green solid mass, soluble in acids (Vauquelin). Lefort (Jahresb. 1861, p. 206), by precipitating a dilute neutral solution of a barium-salt with a dilute solution of the salt $2Na^2O.9SiO^2$ (p. 248), obtained a trisilicate of barium, $Ba''O.3SiO^2.3H^2O$; v. Ammon (*ibid.* 1862, p. 140), by precipitation with sodic monosilicate, obtained the salt $Ba''O.SiO.^2$

Silicates of Calcium. The compounds $2Ca''O.SiO^2$, $2Ca''O.3SiO^2$, $Ca''O.2SiO^2$, and $Ca''O.3SiO^2$, are produced by exposing mixtures of quartz and marble, in the proper proportions, to the full heat of a smith's forge: the first does not fuse, but merely bakes together; the other three are more fusible. A silicate of calcium is precipitated on mixing a solution of any calcium-salt with silicate of potassium or sodium (p. 249). Lefort obtained by precipitation, as above, the salt $2Ca''O.9SiO^2.3H^2O$; v. Ammon obtained the monosilicate $Ca''O.SiO^2$.

Silicate of calcium forms the essential constituent of hydraulic mortars which harden under water. This kind of mortar is produced by mixing pure lime slaked to a paste with water and silica or silicious materials in such a state that the silica can unite with the lime in the wet way. A mixture of lime with pounded quartz or fine sand does not harden under water. Such a mixture, in fact, constitutes ordinary mortar, which hardens only on exposure to the air, partly by drying, partly from absorption of carbonic acid. But if pounded opal or precipitated silica be substituted for the quartz, combination takes place, and the mixture hardens under water. More complete hardening is, however, obtained by mixing lime with certain silicious minerals, called *natural cements*—viz., the pozzolana of Naples and other volcanic districts (iv. 724), the tufa-stone (called *trass* in the pulverised state) found abundantly in valleys in the North of Ireland, among the schistose formations on the banks of the Rhine, and at Monheim in Bavaria,—also pumice, basalt-tuff, and slate-clay. All these substances consist mainly of hydrated silicates of aluminium with a large proportion of silica and smaller quantities of lime, magnesia, oxide of iron, and alkalis. Tufa-stone contains 57·0 per cent. silica, 16·0 clay, 2·6 lime, 1·0 magnesia, 7·0 potash, 1·0 soda, 5 oxides of iron and titanium, and 9·6 water. When any of these materials are mixed with lime and water, silicate and aluminate of calcium are formed—sometimes also silicates of magnesium and iron, which assume a stony hardness. *Marl*, which is a mixture of clay with carbonate of calcium, forms a natural hydraulic limestone. It is best adapted for the purpose when it contains 1 pt. of clay to 3 pts. of calcic carbonate. When such a mixture is ignited, silicate and aluminate of calcium are formed, and the pulverised product hardens readily under water. If the clay is in much smaller proportion than the above, a cement must be added after burning and slaking the lime; if, on the other hand, the marl contains too much clay, pure slaked lime must be added. The silicious nodules, or septaria, found in the Isle of Sheppey and elsewhere on the English coast, which consist of silicious clay intersected by veins of calcspar, also yield when calcined a hydraulic mortar, known as *Roman* *cement.* Artificial mixtures of chalk or lime with clay or pulverised flint, yield similar products when burnt in a kiln. (See *Gmelin's Handbook*, iii. 390; and *Ure's Dictionary of Arts*, &c. iii. 200.)

Natural Silicates of Calcium.—a. Monosilicate or *Metasilicate*, $Ca''SiO^3 = Ca''O.SiO^2$, Wollastonite, or Tabular Spar, occurs in monoclinic crystals (of specific gravity = 2·78—2·9, and hardness = 4·5—5) in the Bannat, at Pargas in Finland, Konigsberg in Norway, on the Castle Rock, Edinburgh, in basalt, and in lava at Capo di Bove, near Rome.

β. Sesquisilicate, $2Ca''O.3SiO^2.\frac{8}{3}H^2O$. This is essentially the composition of gyrolite or gurolite (ii. 963).

Disilicate, $Ca''Si^2O^5.2H^2O = Ca''O.2SiO^2.2H^2O$. Okenite (iv. 191).

Silico-borate of Calcium, $Ca''Si^2O^5.Ca''B^2O^4$, occurs with 1 at. water as datholite (ii. 305), and with 2 at. water as botryolite (i. 651).

Silico-titanate of Calcium, $Ca''Si^3O^7.2Ca''TiO^3$, occurs as sphene (*q. v.*)

Silicate of Cerium, $2Ce''O.SiO^2$. Cerite (i. 831) has this composition, the cerium being partly replaced by lanthanum, didymium, calcium, and iron.

Silicate of Cobalt. The aqueous solution of potassic or sodic disilicate forms a beautiful blue precipitate with cobalt-salts (Fuchs). The solution of the tetrasilicate forms no precipitate.

Silicates of Copper. *a. Monosilicate.*—Two cupric minerals are known having the composition of cupric monosilicate with different proportions of water—viz., dioptase, $Cu''SiO^3.H^2O$ (already described, ii. 335), and chrysocolla, $Cu''SiO^3.2H^2O$. The latter occurs, accompanying other copper ores, in Cornwall, Hungary, and other localities, in botryoïdal or massive forms, also encrusting and disseminated. Hardness = 2 – 3. Specific gravity = 2—2·238. It has a mountain-green or bluish-green colour, passing into sky-blue, with vitreous or earthy lustre, and is translucent in various degrees, or opaque. Fracture conchoïdal. Rather sectile; translucent varieties brittle.

Analyses of Chrysocolla.—a. From Stromsheien in Satersdälen, Norway (Scheerer, Pogg. Ann. lxv. 289).—*b.* From Lake Superior (*Rammelsberg's Mineralchemie*, p. 351):

	SiO^2.	CuO.	Fe^2O^3.	CaO.	MgO.	H^2O.		
a.	35·14	43·07	1·09	. .	. .	20·36	=	99·66
b.	32·55	42·32	1·63	1·76	1·06	20·68	=	100

The formula $CuO\ SiO^2.2H^2O$ requires 34·83 silica, 44·82 cupric oxide, and 20·35 water.

Plattner's *Kupferblau*, from the Herrensegen mine in Baden, containing 45·5 per cent. cupric oxide, also belongs to this place.—A more highly hydrated cupric monosilicate, containing $Cu''SiO^3.4H^2O$ (according to Nordenskiold, 31·45 per. cent. SiO^2, 37·31 CuO, 0·40 FeO, and 31·18 water), occurs at Nischne-Tagilsk in Siberia: it gives off about three-fourths of its water at 100°.

The chrysocollas of Siegen and of Canaveilles near Prades in the Pyrenees, also the blue copper from the Turjinian mines in the Ural, are mixtures of cupric silicate and carbonate.—*Copper pitchblende*, a brown scoriaceous mineral from the same mines, is a mixture of chrysocolla and brown hæmatite; a similar mineral, from Zomelahuacan in Mexico, has the composition of a hydrated cupric disilicate, $CuO.2SiO^2.4H^2O$, mixed with brown hæmatite.

β. Sesquisilicate, $2Cu''O.3SiO^2.6H^2O$?—This appears to be the composition of a mineral from Somerville, New Jersey, analysed by Berthier, and from Chili, analysed by Kittredge:

	SiO^2.	CuO.	FeO.	CaO.	MgO.	H^2O.		
New Jersey	35·4	35·1	. .	. .	. .	28·5	=	99·0
Chili	40·09	27·97	4·94	1·49	0·78	24·73	=	100

The formula requires 40·89 SiO^2, 35·08 CuO, and 24·03 water.

Among cupric silicates must also be enumerated demidoffite, a mineral occurring as a thin blue coating on malachite at Nischne-Tagilsk, and containing, according to Nordenskiold, 10·22 per cent. P^2O^5, 31·35 SiO^2, 33·14 CuO, 3·15 MgO, 0·5 Al^2O^3, and 23·03 water. (*Rammelsberg's Mineralchemie*, p. 533.)

Silicate of Didymium. See Cerite (i. 831).

Ferrous Silicates.—*a.* $\overset{''}{Fe}{}^2SiO^4 = 2Fe''O.SiO^2$.—This is the composition of Fayalite or iron-chrysolite (ii. 617); also, approximately, that of some of the refinery-slags obtained in the conversion of cast into malleable iron (iii. 351), and in the refining of coarse copper. (*Gmelin's Handbook*, v. 278.)

β. Monosilicate, $Fe''SiO^3 = Fe''O.SiO^2$.—Grunerite, an asbestiform mineral from Collobrières, has this composition.—A black augite from Arendal, specific gravity = 3·467, is a calcio-ferrous monosilicate, containing, according to Wolff (J. pr. Chem. xxxiv. 236), 47·78 per cent. SiO^2, 23·95 CaO, and 27·01 FeO, agreeing nearly with the formula $\left.\begin{matrix}\frac{1}{2}Ca''O\\ \frac{1}{2}Fe''O\end{matrix}\right\}SiO^2$.

γ. *Tetrasilicate?* A solution of ferrous chloride in less than 2,500 pts. of water gives a greyish-green precipitate with tetrasilicate of sodium. (Walker.)

Silicates of Lanthanum. See Cerite (i. 381).

Silicates of Lead. Silica melts with lead-oxide to a yellow glass. Silicate of lead is also precipitated on adding ammonia to silicofluoride of lead.—A *borosilicate of lead* is obtained by fusing 112 pts. lead-oxide with 16 pts. silica and 24 boric anhydride, as a yellow glass, which melts less easily than borate of lead, but more easily than flint-glass, and is strongly tarnished by immersion in sulphydric acid gas. (Faraday.)

Silicate of Glucinum. $\overset{\prime\prime}{G}{}^2SiO^4 = 2G''O.SiO^2$. Phenacite (iv. 387).

Silicates of Magnesium. α. $8Mg''O.3SiO^2$.—Chondrodite (i. 930) is represented by this formula, the oxygen being, however, partly replaced by fluorine, and the magnesia in most cases partly by ferrous oxide.

β. $Mg^2SiO^4 = 2Mg''O.SiO^2$.—This is the composition of chrysolite and olivin (iv. 201), the magnesium being always more or less replaced by iron. Forsterite, from Monte Somma, exhibits the nearest approach to a pure magnesic orthosilicate, containing only 2·33 ferrous oxide. In the other varieties of olivin, the ferrous oxide varies from 3 to about 20 per cent.—Monticellite, a rare mineral occurring on Somma in yellow-grey crystals, of specific gravity 3·119, contains, according to Rammelsberg (*Mineralchemie*, p. 442), 37·89 per cent. silica, 34·92 lime, 22·04 magnesia, and 5·61 ferrous oxide, agreeing with the formula $\overset{\prime\prime}{Ca}{}^2SiO^4.\left.\begin{matrix}\frac{7}{8}Mg''\\ \frac{1}{8}Fe''\end{matrix}\right\}^2SiO^4$. Batrachite, a massive mineral, of specific gravity 3·033, from the Rizoniberg in the Southern Tyrol, appears to have the same composition.

γ. $3Mg''O.2SiO^2.2aq. = \overset{\prime\prime}{Mg}{}^2SiO^4.Mg''SiO^3.2aq.$—This is the composition of serpentine (p. 236), the magnesia being replaced by ferrous oxide to the extent of 0 to 13·5 per cent. Pure magnesian serpentine is found at Gullsjö, in Wermeland, Sweden. Small quantities of soda, manganous oxide, and nickel-oxide are also occasionally present, and in many varieties the silica is replaced to a small amount by alumina.—Vorhauserite from Monzoni, in the Tyrol, is a serpentine containing 3 at. water.—Thermophyllite from Hopoovaara in Finland appears, from Arppe's analysis, to have the composition $2(3MgO.2SiO^2).3aq.$; but other analyses give different results. (See Thermophyllite.)

δ. $4Mg''O.3SiO^2 = \overset{\prime\prime}{Mg}{}^2SiO^4.2Mg''SiO^3$.—This formula with 6 at. water represents the composition of gymnite or deweylite (ii. 312). Hydrophite or Jenkinsite (iii. 212) is the same with 4 at. water, and $\frac{2}{5}$ of the magnesium replaced by iron. Thermophyllite, according to Northcote (J. pr. Chem. lxxvi. 253), is also a $\frac{3}{4}$-silicate of magnesium with 2 at. water.

ε. $Mg''O.SiO^2 = Mg''SiO^3$.—This formula, with the magnesia more or less replaced by ferrous oxide, manganous oxide, and lime, and the silica sometimes by alumina, represents the composition of the several varieties of augite and hornblende (i. 475; iii. 167). These two mineral species differ in crystalline form: they are both monoclinic, but differ in their angles:

	a : *b* : *c*.	Angle *b* : *c*.	Angle ∞P : ∞P.
Augite	0·9136 : 1 : 0·5399	74° 1′	92° 54
Hornblende	1·837 : 1 : 0·5401	75° 10′	55° 30′

The replacement of silica by alumina takes place more frequently and to a greater extent in hornblende than in augite; many aluminiferous hornblendes also contain ferric oxide, being, according to Rammelsberg, mixtures of the isomorphous compounds $M''O.SiO^2$, $Fe^2O^3.3SiO^2$, and $3M''O.2Al^2O^3$ (iii. 170).

The following are hydrated monosilicates of magnesium:—

Aphrodite, $4Mg''SiO^3.3H^2O$.
Picrophyll, $3(\frac{8}{9}Mg.\frac{1}{9}Fe)''SiO^3.2H^2O$
Picrosmin, $2Mg''SiO^3.H^2O$.
Monradite, $4(\frac{6}{7}Mg.\frac{1}{7}Fe)''SiO^3.H^2O$.

Aphrodite contains, according to Berlin's analysis, 51·56 per cent. SiO^2, 0·17 Al^2O^3, 33·90 MgO, 1·55 MnO, 0·57 MnO, and 11·83 water. The analyses of the other three minerals have been given in their alphabetical places.

ζ. $6MgO.7SiO^2$.—This appears to be the composition of an anhydrous talc found in the valley of Chamounix.—Spadaite, a reddish massive mineral, from Capo di

Bove, containing 56·00 SiO^2, 0·66 Al^2O^3, 30·67 MgO, 0·66 FeO, and 11·34 water, may be approximately represented by the same formula with 5 at. water, or by $5Mg''O.6SiO^2 + 4aq$. (*Rammelsberg's Mineralchemie*, p. 520.)

η. $4Mg''O.5SiO^2 = 4Mg''SiO^3.SiO^2$.—This, with $\frac{3}{4}$ at. water, is the composition of talc, a small portion of the magnesia being replaced by ferrous oxide.

θ. $2Mg''O.3SiO^2 = 2Mg''SiO^3.SiO^2$.—This, with 2 at. and 4 at. water, is the composition of meerschaum. The same formula with 12 at. water, and $\frac{2}{7}$ of the magnesia replaced by ferrous oxide, gives the composition of chlorophæite.

Silicates of Manganese. α. $2Mn''O.SiO^2 = \overset{''}{Mn}{}^2SiO^4$.—Tephroite, from Sparta, New Jersey, has this composition, with a small portion of the manganese replaced by iron.—Knebelite, from Ilmenau and from Dannemora in Sweden, consists of $(Mn''.Fe'')^2SiO^4$.—Troostite, from Sterling, New Jersey, is an orthosilicate, containing manganese and zinc, with small quantities of iron and magnesium.

β. $Mn''O.SiO^2 = Mn''SiO^3$.—Rhodonite is a manganous augite, containing also calcium, iron, and magnesium (p. 107).—Fowlerite and Jeffersonite are similar in composition, but also contain zinc.

Silicates of Mercury. Tetrasilicate of sodium gives a white precipitate with mercurous nitrate. It does not precipitate mercuric chloride, but the mixed solution yields very small dark crystals on evaporation, or even without evaporation if it is concentrated. (*Gmelin's Handbook*, v. 110.)

Silicates of Molybdenum. Molybdous and molybdic silicofluoride yield with ammonia, dark-brown flocks, from which the ammoniacal solution gradually removes the oxide of molybdenum, leaving pure silica. (Berzelius.)

Silicates of Nickel. See PIMELITE (iv. 647). Nickel-gymnite is a hydrated silicate of nickel and magnesium, containing $\left.\begin{matrix}\frac{1}{2}Ni''O\\ \frac{1}{2}Mg''O\end{matrix}\right\}^4.3SiO^2.6aq$.

Silicates of Potassium and Sodium (pp. 247-251).—Monosilicate of sodium may be obtained in well-defined monoclinic prisms containing $Na^2SiO^3.8H^2O$, by digesting ignited silica with an equivalent quantity of crude soda-ley, evaporating out of contact with air, till small crystals of sodic carbonate separate, cooling the remaining syrup to −22°, stirring with a glass rod till it solidifies to a crystalline pulp, redissolving in water, and leaving the solution to stand. The solution of this salt yields, with barium and calcium-salts, precipitates containing $Ba''SiO^3$ and $Ca''SiO^3$ respectively, and with magnesium-salts, a precipitate containing $3Mg''SiO^3.5H^2O$. (v. Ammon.)

Silicate of Strontium. One part of silica fuses, with an equal weight of strontia, partly to an amber-coloured glass, and partly to a black and white enamel (Kirwan). With 3 parts of strontia it forms a solid, grey, sonorous mass, which is nearly tasteless, and dissolves but sparingly in water, though readily in aqueous acids (Vauquelin). Carbonate of strontium, digested in solution of silica, is converted into dense hydrated silicate of strontium. (Kuhlmann.)

Silicate of Thorinum, $3\overset{''}{Th}{}^2SiO^4.4H^2O$. Thorite (*q.v.*).

Silicate of Yttrium. Gadolinite is an orthosilicate of yttrium, cerium, and iron $(Y'';Ce'';Fe'')^2SiO^4$.

Silicate of Zinc. The orthosilicate, $\overset{''}{Zn}{}^2SiO^4$, occurs anhydrous as willemite, hydrated as silicious calamine or zinc-glance, $\overset{''}{Zn}{}^2SiO^4.H^2O$ (i. 714). Troostite from Sterling, New Jersey, is an orthosilicate of zinc, manganese, magnesium, iron, and calcium. Fowlerite and jeffersonite are augitic minerals containing small quantities of zinc.

Silicates containing Triatomic Metals: Silicates of Sesquioxides.

Silicates of Aluminium. α. $2Al^2O^3.SiO^2$.—This, with 9 at. water, is the composition of collyrite (i. 1084), from Schemnitz in Hungary (Klaproth, *Beiträge*, i. 257), and from Esquerra in Spain (Berthier, Ann. Ch. Phys. [2] xxxii. 332):

	Calculation.		*Schemnitz.*	*Esquerra.*
SiO^2	60	13·85	14	15·0
$2Al^2O^3$	151	45·94	45	44·5
$9H^2O$	162	40·21	42	40·5
$2Al^2O^3.SiO^2.9aq.$	373	100·00	101	100·0

A mineral called collyrite, from Weissenfels in Saxony, has the composition $Al^2O^3.SiO^2.5aq.$ like the allophanes; another, occurring in alum-slate, contains

$8Al^2O^3.9SiO^2.54aq.$, like some varieties of staurolite (*infra*).—Schrötterite or opaline allophane, from Freienstein in Styria—having a density of 1·985 to 2·015, greenish-white colour, vitreous lustre, and conchoïdal fracture—contains, according to Schrötter (J. pr. Chem. xi. 380), 11·94 SiO^2, 46·29 Al^2O^3, 2·80 Fe^2O^3, 1·16 CaO, 0·25 CuO, 0·63 SO^3, and 35·85 water, agreeing approximately with the formula $5Al^2O^3.2SiO^2.20aq.$, which is more basic than that of collyrite; but the mineral is probably a mixture containing hydrate of aluminium.

β. $4Al^2O^3.3SiO^2$.—This formula, with the alumina partly replaced by ferric oxide, represents the composition of some varieties of staurolite from the St. Gothard, a mineral which crystallises in trimetric prisms, having the axes $a : b : c = 1 : 2·1123 : 1·4478$, and the angle $\infty P : \infty P = 129° 20'$. Observed combination $\infty P . \infty\breve{P}\infty . . \infty\bar{P}\infty . oP$. Cleavage parallel to $\infty\breve{P}\infty$, distinct but interrupted; parallel to ∞P, in traces. The crystals are thick and often cruciform, translucent or opaque, with brown colour, subvitreous lustre inclining to resinous, and conchoïdal fracture. Hardness = 7—7·5. Specific gravity = 3·5—3·75.

Analyses.—*a*. Red (Klaproth, *Beitr.* v. 80).—*b*. Dark-red: specific gravity = 3·737—3·741 (Lohmeyer, s. Jacobson).—*c*. (Rosales, *ibid.*)—*d*. Marignac (Ann. Ch. Phys. [3] xiv. 9).—*e*, *f*, *g*, *h*. Jacobson (Pogg. Ann. lxii. 419; lxviii. 414):

	Calculation.		Analyses.							
			a.	*b*.	*c*.	*d*.	*e*	*f*.	*g*.	*h*.
$3SiO^2$	180·00	28·15	27 00	27·02	27·25	28·47	29·13	29·72	30·31	30·91
$\frac{10}{3}Al^2O^3$	343·33	54·02	52 25	49·96	56·39	53·34	52·01	54·72	46 80	48·68
$\frac{2}{3}Fe^2O^3$	106·67	16·83	18·50	20 07	19·37	17·41	17·58	15·60	18·08	15·37
Manganic oxide	. .	. .	0·25	0·28	. .	0·31	. .	. .	0·13	1·19
Magnesia	. .	. .	. .	. .	2·57	0·72	1·28	1·85	2·16	1·33
$\left.\begin{matrix}\frac{5}{6}Al^2O^3\\ \frac{1}{6}Fe^2O^3\end{matrix}\right\} .3SiO^2$	630·00	100·00	98·0	97·33	105·58	100·25	100·00	101·98	97·48	97·48

Dillnite (ii. 331) is a hydrated $\frac{3}{4}$-silicate of aluminium, $4Al^2O^3.3SiO^2.9aq.$, containing small quantities of lime and magnesia, but no ferric oxide.

γ. $10Al^2O^3.9SiO^2$. Staurolite from Airolo on the St. Gothard: specific gravity = 3·66—3·73.

	Calculation.		Jacobson.	
$9SiO^2$	540·00	33·06	33·45	32·99
$\frac{25}{3}Al^2O^3$	858·33	51·04	47.23	47·92
$\frac{5}{3}Fe^2O^3$	171·67	15·90	16·51	16·65
Magnesia	. . .	. .	1·99	1·66
$\left.\begin{matrix}\frac{5}{6}Al^2O^3\\ \frac{1}{6}Fe^2O^3\end{matrix}\right\}^{10} .9SiO^2$	1570·00	100·00	99·18	99·22

δ. $Al^2O^3.SiO^2$.—Under this formula are included andalusite (i. 291), cyanite or kyanite (iii. 449), sillimanite, and a few other minerals, apparently produced by alteration of these. Topaz (*q. v.*) consists of the same silicate in isomorphous mixture with aluminic silicofluoride. Allophane is the same silicate with 5 or 6 at. water.

Analyses.—1. Andalusite.—*a*. Brazil (Damour).—*b*. Robschütz, near Meissen in Saxony: reddish, harder than quartz: specific gravity = 3·11 (Pfingsten).[*]—*c*. Bräunsdorf, near Freiberg: reddish: specific gravity = 3·07 (Pfingsten).—*d*. Lisens in the Tyrol; specific gravity = 3·401. (Roth.)

2. Cyanite.—*e*. St. Gothard (Rosales).—*f*. The Sau Alp in Carinthia (Köhler).—*g*. Elfdal in Wermland: specific gravity = 3·8 (Igelström):

	Calculation.		Andalusite.				Cyanite.		
			a.	*b*.	*c*.	*d*.	*e*.	*f*.	*g*.
SiO^2	60	37 5	37·03	36·84	37·37	36·74	36 67	37·92	40·02
Al^2O^3	103	62·5	61·45	55·82	59·88	59·65	63·11	61·60	58·46
Ferric oxide	. .	. .	1·17	3·22	1·33	2·80	1·19	1·04	2·04
Lime	. .	. .	. .	1·09	0·61	0·49	. .	0·42	
Magnesia	. .	. .	. .	1·14	0·17				
$Al^2O^3.SiO^2$	163	100·0	99·65	98·11	99·56	99·68	100 97	100·98	100·52

In andalusite from Lisens, Bunsen found 40·17 per cent. silica and 58·62 alumina; A. Erdmann, 39·99 silica and 58·60 alumina, agreeing more nearly with $8Al^2O^3.9SiO^2$, which requires 40·3 silica and 59·7 alumina.

3. Sillimanite.—*h*—*m*. Saybrook, Chester County, Connecticut: *h*, Thomson; *i*, Bowen; *j*, Hayes; *k*, B. Silliman; *l*, Staaf; *m*, Connel; *n*, Fairfield, New York. (Norton.)

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[*] For references, see *Rammelsberg's Mineralchemie*, pp. 558, 560, 562.

4. Talc-lithomarge; *o.* Rochlitz in Saxony (Korsten).—*p.* Zeidover, near Temesvar in Hungary (Kussin):

	Sillimanite.							Talc-lithomarge.	
	h.	*i.*	*j.*	*k.*	*l.*	*m.*	*n.*	*o.*	*p.*
SiO^2.	45·65	43 00	42·60	37·65	37·36	36·75	37·70	37 62	36 01
Al^2O^3	49·50	54·21	54·90	62·41	58 62	58·95	62·75	60·50	63·72
Ferric oxide . . .	4·55	2·00	1·10	. .	2·17	0·99	2·28		
Manganic oxide . .	. .	. .	. .	. .	. .	. .	. .	0·63	
Magnesia	. .	. .	0·71	. .	0·40				
Water	. .	0·51	. .	. .	0·43	. .	. .	0·82	
	99·70	99·72	99·31	100·06	98·98	96·69	102·73	99·57	99·73

Monrolite from Monroe, New York, exhibits the same characters and nearly the same composition as cyanite, but gives off from 1 to 2·5 per cent. water when heated; specific gravity = 3·04—3·09. Wörthite, a mineral occurring near St. Petersburg in white translucent fragments, infusible before the blowpipe, has also nearly the same composition. Both minerals doubtless result from the alteration of cyanite.

Bucholzite from Faltigl in the Tyrol and Chester County, Pennsylvania, Fibrolite from the Carnatic and from Delaware, and Xenolite, found near St. Petersburg, are fibrous minerals, which appear also to have been produced by the alteration of cyanite, sillimanite, or andalusite, but they are probably sometimes also mixed with quartz. The older analyses by Thomson, Brandes, and others, give for these minerals from 40·05 to 47·44 per cent. silica, and 58·88 to 50·0 alumina, agreeing approximately with the formula $2Al^2O^3.3SiO^2$, but the more recent analyses by B. Silliman (Sill. Am. J. [2] viii. 10), give 35·13—36·31 silica, and 64·93—62·42 alumina, which is the same as that of cyanite, &c. Xenolite forms prisms of 91°, which seems to show that it has been formed from andalusite.

Chiastolite or Hollow spar (i. 868) is an andalusite varying greatly in hardness and composition, and usually enclosing masses of rock, found in Spain, at Bona in Algeria, at Lancaster in Massachusetts, and in Bretagne.

5. Allophane.—*a.* Friesdorf, near Bonn (Bunsen).—*b.* New Charlton, near Woolwich (Northcote).—*c.* Bleiberg in the Eifel (Bergemann).—*d.* Gersbach, in the Black Forest (Walchner).—*e.* Richmond, Massachusetts (B. Silliman).—*f.* New Charlton (Woolwich).—*g.* Goldhausen, near Corbach, Waldeck: light-coloured. —*h.* The same, dark-coloured: specific gravity = 2·02 (Schnabel).—*i.* Schneeberg (Ficinus):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Carbonic anhydride	. .	2·73	1·24	. .	. .	2·44	. .	. .	1·2
Silica . . .	22·30	20·50	19·35	21·11	22·65	19·58	24·19	19·41	30·0
Alumina . . .	32·18	31·34	32 75	38·76	38·77	37·30	25·80	26·77	16 7
Ferric oxide . .	2 90	0·31	0 30	. .	. .	0·11			
Cupric oxide . .	. .	. .	2 57	2·33	. .	1·36	13·71	18·97	19·2
Manganic oxide .	. .	. .	. .	. .	. .	. .	. .	. .	1·8
Lime . . .	. .	1·92	1·58	. .	2·83*	. .	. .	. .	1·5
Water . . .	42·62	42·91	40·23 0·87†	35·75	35·24	39·19	35·49	34·72	29·9
	100·00	99·71	98·89	97·95	99·49	99·98	99·19	99·87	100·3

This table shows that the name allophane has been applied to substances differing greatly in constitution. The analyses *a*, *b*, *c* may be represented approximately by the formula $Al^2O^3.SiO^2.6aq.$ (22·14 SiO^2, 38·01 Al^2O^3, 39·85 H^2O); *d*, *e*, *f* by $Al^2O^3.SiO^2.5aq.$ (24·34 SiO^2, 40·35 Al^2O^3, 35·31 H^2O). Both varieties are often mixed with calcic carbonate and cupric silicate; in the latter case they have a blue colour. The more highly cupriferous allophanes, *g*, *h*, *i*, are mixtures of hydrated aluminic silicate and cupric silicate.

Chrome-ochre, Miloschin, and Wolchonskoïte, are chromiferous clays of very variable composition. The first contains from 46 to 64 per cent. silica, 22·5 to 30·5 alumina, 4 to 10·5 chromic oxide, and 6·25 to 12·5 water; the second, from Rudniak in Servia, 27·5 per cent. silica, 45 01 alumina, 3·61 chromic oxide, and 22·30 water; the third, from Kreis Ochansk, in the government of Perm, Russia, 27 to 37 per cent. silica, about 6·5 alumina, 18 to 34 chromic oxide, 7 to 10 ferric oxide, 21·84 water, with small quantities of lime, magnesia, and manganous oxide.

Collyrite, from Weissenfels, containing, according to Kersten, 23·3 per cent. silica, 42·8 alumina, and 34·7 water, is also represented most nearly by the formula $Al^2O^3.SiO^2.5aq.$

ε. $8Al^2O^3.9SiO^2$.—Staurolite, from Polewskoi, in the Ural, contains, according to Jacobson, 38·33—38·68 per cent. SiO^2, 45·97—47·43 Al^2O^3, 14·60—15·06 Fe^2O^3, and 2·44—2·47 magnesia, agreeing nearly with the formula $\left.\begin{matrix}\frac{5}{6}Al^2O^3\\ \frac{1}{6}Fe^2O^3\end{matrix}\right\}^8.9SiO^2$. (Compare p. 255.)

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* Magnesia.

† Quartz and Gypsum.

Collyrite, occurring in alum-slate, contains, according to **Anthon** (Berz. Jahresb. xxiii. 280), 24·2 per cent. SiO^2, 34·5 Al^2O^3, and 41·3 water, agreeing approximately with the formula $8Al^2O^3.9SiO^2.54aq$.

ζ. $5Al^2O^3.6SiO^2$.—**Staurolite**, from Bretagne (specific gravity = 3·527—3·529), contains, according to Jacobson, 39·19—40·35 per cent. SiO^2, 44·87—44·22 Al^2O^3, 15·09—15·77 Fe^2O^3, 0·17—0·10 Mn^2O^3, and, in one specimen, 0·32 magnesia, which may be represented by the formula—$\left.\begin{matrix}\frac{5}{6}Al^2O^3\\ \frac{1}{6}Fe^2O^3\end{matrix}\right\}^5.6SiO^2$.

η. $2Al^2O^3.3SiO^2$.—This, with various quantities of water, represents approximately the composition of **porcelain clay**, from Gutenberg, near Halle (**Bley**, J. pr. Chem. v. 313), and of **pholerite** (i. 496), near Fins, Dept. de l'Allier (**Guillemin**, Ann. Min. xi. 489), and from Naxos (**Smith**, ibid. [4], xviii. 299).

Clay from Gutenberg.			Bley.
$3SiO^2$ . .	180	40·91	39·62
$2Al^2O^3$ . .	206	46·82	45·00
$3H^2O$ . .	54	12·27	10·00
$CaCO^3$ . .	. .	. .	0·07
$MgCO^3$ . .	. .	. .	3·32
Mn^2O^3 . .	. .	. .	0·19
$2Al^2O^3.3SiO^2.3aq.$	440	100·00	98·20

Pholerite.			Guillemin.	Smith.
$3SiO^2$ . .	180	39·30	41·65	44·41
$2Al^2O^3$ . .	206	44·98	43·35	41·20
$4H^2O$ . .	72	15·72	15·00	13·14
CaO . . .	. .	. .	. .	1·21
$2Al^2O^3.3SiO^2.4aq.$	458	100·00	100·00	99·96

Plinthite, from the county of Antrim, in Ireland, contains, according to **Thomson** (*Outlines*, i. 323), 30·88 per cent. silica, 20·76 alumina, 26·16 ferric oxide, 2·6 lime, and 19·96 water, and may be represented by the formula $2(Al^2O^3;Fe^2O^3).3SiO^2.6aq$.

Carpholite, from the Schlackenwald, in Bohemia (i. 806), has a composition represented by the formula $2(Al^2O^3;Mn^2O^3;Fe^2O^3).3SiO^2.3aq$.

θ. $3Al^2O^3.5SiO^2$.—**Lenzinite**, from La Vilate, in France (iii. 571), and that from Koll, in the Eifel, containing, according to John, 37·5 per cent. silica, 37·5 alumina, and 25·0 water, are approximately represented by the formula $3Al^2O^3.5SiO^2.11aq.$; the same name is, however, applied to a clay containing a much larger proportion of silica.

ι. $Al^2O^3.2SiO^2$.—This, with 2 at. water, represents the composition of nearly all varieties of **kaolin**, or **porcelain-clay**. The numerous analyses of this substance yield on the average about 47 per cent. silica, 40 alumina, and 13 water, the formula $Al^2O^3.2SiO^2.2aq.$ requiring 47·05 silica, 39·21 alumina, and 13·74 water. The following are examples:—

a. Aue near Schneeberg (**Forchhammer**, Pogg. Ann. xxxv. 331).—*b.* Morl near Halle (**Forchhammer**).—*c.* Altenberg in the Erzgebirge: a pseudomorph after prosopite (**Scheerer**, Pogg. Ann. ci. 361).—*d.* St. Yrieux near Limoges (**Forchhammer**).—*e.* St. Yrieux: produced by weathering of beryl (**Damour**, Bull. geolog. [2] vii. 224).—*f.* Cornwall (**Brown**, J. pr. Chem. xliv. 232).—*g.* Rio Janeiro (**Kussin**, Ramm. Mineralch. p. 574).—*h*, *i*. China: *h* from Tonkang, *i* from Sykang (**Ebelmen** and **Salvétat**, Ann. Ch. Phys. [3] xxxi. 257):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Silica . . .	46·53	46·80	45·63	48·68	45·61	46·29	45·37	50·5	55·3
Alumina . .	39·47	36·83	39·89	36·92	38·86	40·09	34·27	33·7	30·3
Ferric oxide . .	. . .	3·11	. .	. .	0·94	0·30	. .	1·8	2·0
Lime . . .	. . .		0·60	. .	1·10*	0·50	. .	. .	. .
Magnesia . .	. . .	0·27	. .	0·52	. .	. .	. .	0·8	0·4
Potash . . .	. . .	. . .	. .	. .	. .	. .	. .	1·9	1·1
Soda . . .	. . .	. . .	. .	0·58	. .	. .	. .	. .	2·7
Water . . .	13·97	12·44	13·70	13·13	14·04	12·67	20·01	11·2	8·2
Calcic carbonate .	0·31	0·55							
	100·28	100·00	99·82	99·83	100·55	99·85	99·65	99·9	100·0

Kaolin is produced by the decomposition of orthoclase, $K^2O.Al^2O^3.6SiO^2$, which under the influence of water containing carbonic acid, or sulphuric acid resulting from the oxidation-pyrites, loses its potash and two-thirds (4 at.) of its silica, and at the same time takes up 2 at. water. Some varieties of kaolin have, however, a different composition: thus that of Gutenberg, as already observed, is nearly $2Al^2O^3.3SiO^2.3aq.$, and that of Passau—which, according to Fuchs, is produced by the decomposition of porcelain-spar—is, according to Forchhammer, $4Al^2O^3.9SiO^2.12aq$. [For analyses of **fire-clays**, see ii. 653.]

Lithomarge (i. 730) is a name applied to a number of aluminous silicates, most of which have nearly the composition of porcelain-clay.

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* Glucina.

Analyses: *a.* Rochlitz, in Saxony: compact (Klaproth).*—*b.* Buchberg, near Landshut, in Silesia (Zellner).—*c.* Clausthal: white, phosphorescent; specific gravity = 1·59 (Dumenil).—*d.* Rumpelsberg, near Auerbach: from topaz rock; crystalline under the microscope: specific gravity = 2·6 (Clark).—*e.* Schlackenwald, Bohemia: radiate; glows brightly before the blowpipe; not decomposible by hydrochloric acid (Rammelsberg).—*f.* *Tucsite*, from the Tweed (1) Thomson; (2) Richardson:—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.* (1).	*g.* (2).
Silica . . .	45·25	49·2	43 00	47·33	47·26	43·46	44 30	43·80
Alumina . .	36·50	36·2	40·25	40·23	39·02	41·48	40·40	40·10
Ferric oxide .	2·75	0·5	0·48	. .	. .		. .	0·94
Lime.	. .	. .	0·47	1·44	. .	1·20	0·75	0·64
Magnesia . .	. .	. .	. .		0·89	0·37†	0·50	0·55
Water . . .	14·00	14·0	15·50	12·36	13·55	13·49	13 50	14 21
	98·50	99·9	99·70	101·36	100·72	100·00	99·45	100·21

The following varieties are distinguished by containing a considerable amount of potash:—*h.* Green lithomarge, from St. Zorge in the Harz: specific gravity = 3·086 (Rammelsberg).—*i.* Lithomarge from Schlackenwald (Krieg):—

	SiO^2.	Al^2O^3.	Fe^2O^3.	CaO.	MgO.	K^2O.	Na^2O.	H^2O.		
h.	49·75	29·88	6·61	0·43	1·47	6·35	. .	5·48	=	99·97
i.	52·40	31·94	1·23	. .	1·44	5·41	1·73	5·00	=	99·15

Ferruginous lithomarge from Planitz, near Zwickau in Saxony, contains, according to Schüler, 41·66 per cent. silica, 22·85 alumina, 12·98 ferric oxide, 1·68 manganic oxide, 3·04 lime, 2·55 magnesia, 0·93 potash, and 14·20 water, which may be represented by the formula $(Al^2O^3; Fe^2O^3) 2SiO^2$.

Halloysite (iii. 7) has sometimes the composition of kaolin or lithomarge; some varieties, however, contain a larger quantity of water, agreeing with the formula $Al^2O^3.2SiO^2 4aq$. The latter formula also represents nearly the composition of some kinds of **bole** (i. 618).

κ. $4Al^2O^3.9SiO^2$.—This formula, with 12 at. water, represents porcelain-clay from Passau, containing, according to Forchhammer, 45·14 per cent. silica, 35·00 alumina, 2·70 ferric oxide and lime, and 18·50 water. The same formula, with 18 at. water, and the alumina partly replaced by ferric oxide, gives the composition of most varieties of **bole**.

λ. $Al^2O^3.3SiO^2$.—This formula, with 3 at. water, represents **razoumoffskin**, an argillaceous mineral from Kosemütz in Silesia (p. 78); also **pyrophyllite** (iv. 769), if the small quantity of protoxides be left out of consideration.

μ. $2Al^2O^3.9SiO^2$.—**Cimolite** (i. 964) is represented by this formula, generally with 6 at., but occasionally with 4 at. water. **Anauxite** (i. 288), from Bilin in Bohemia—containing, according to Plattner, 55 per cent. silica, a large quantity of alumina, 11·5 per cent. water, with small quantities of magnesia—is probably a variety of cimolite.

ν. $Al^2O^3.4SiO^2$.—*a.* **Montmorillonite** (iii. 104), from Montmorillon, Dept. Haute-Vienne; *b.* the same, from Strumbuly in Transylvania; *c.* **Halloysite**, from Confolert, Dept. Charente; *d.* **Lenzinite**, from St. Sevin, Dept. Landes; and *e.* **Bole**, from Michac, Dept. Dordogne, are approximately $Al^2O^3.4SiO^2$ + 2 and 3 at. water; but it is very probable that some of them contain free silica:—

	SiO^2.	Al^2O^3.	Fe^2O^3.	CaO.	MgO.	MnO.	K^2O,Na^2O.	H^2O.			
a.	49·40	19·70	0·80	1·50	0·27	. .	1·50	25·67	=	98·84	Salvétat.
b.	50·04	20·16	0·68	1·46	0·23	. .	1·27	26·00	=	99·84	Damour.
c.	52·40	21·80	. .	2·50	4·28	. .	1·34	17·68	=	100	Hengenau.
d.	49·5	18·0	. .	2·1	2·1	. .	. .	28·0	=	99·7	Berthier.
e.	50·0	22·0	. .	. .	. .	. .	. .	26·0	=	98·0	„
f.	50·55	19·15	. .	0·63	. .	4·40	. .	24·05	=	98·78	v. Hauer.

The last gives off 14·03 per cent. water at 100°. (*Rammelsberg's Mineralchemie*, p. 1014.)

ξ. $Al^2O^3.6SiO^2$?—**Malthacite**, from Steindürfel in the Oberlausitz—containing, according to Meissner (J. pr. Chem. x. 510), 50·2 per cent. silica, 10·7 alumina, 3·1 ferric oxide, 0·2 lime, and 35·8 water—may be approximately represented as $Al^2O^3.6SiO^2.16aq.$, but is probably a mixture.

ο. *Aluminic Silicates of indeterminate composition.*—**Dysyntribite**, from Lawrence County, New York (ii. 368); **Nacrite**, from Brunswick, in the State of Maine, and **Talcite**, from Wicklow in Ireland (iv. 1); **Neurolite**, from Stamstead in Lower Canada (iv. 32); **Portite** from the gabbro of Tuscany (iv. 690); **Rhodalite**, from Ireland, containing, according to Richardson, 55 9 per cent. silica, 11 4 ferric oxide, 8·3 alumina, 1·1 lime, 0·6 magnesia, and 22·0 water; Samoite, from the lava of Upolu (v. 187); Scarbroïte, from Scarborough (v. 204); Smectite, from Cilly in Styria, containing, according to Jordan (Pogg. Ann. lxxvii. 591), 51·21 per cent. silica, 12·25 alumina, 2·07 ferric oxide, 1·89 magnesia, 2·13 lime, and 27·89 water; Smelite, from Telkobanya in Hungary, containing, according to Oswald (J. pr. Chem. xxxv. 39), 50 per cent. silica, 32 alumina, 2 ferric oxide, 2·1 soda, and 13 water; and an earthy mineral from Condé, near Houdan, Dept. Seine et Oise, containing, according to Salvétat (Ann. Ch. Phys. [3] xxxi. 102), 44·5 per cent. silica, 32·5 alumina, 1·2 ferric oxide, 1·02 lime, 0·3 magnesia, 0·4 potash and soda, and 21·7 water.

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* For references, see *Rammelsberg's Mineralchemie*, p. 576.

† Soda.

The following are unctuous clays included under the general denomination of mountain-soaps:—*a*. From Plombières (Berthier, Ann. Min. [3], xi. 479).—*b*. Thüringen (Bucholz, Gehlens N. J. iii. 597).—*c*. Arnstadt, in Thuringia (Ficinus, Schw. J. xxvi. 279).—*d*. Wilhelmshöhe near Cassel (Bechmann, Leonh. Jahrb. 1831, p. 125):—

	P^2O^5.	SiO^2.	Al^2O^3.	Fe^2O^3.	Mn^2O^3.	CaO.	MgO.	H^2O.	Carbon.	Humic acid.	Fossil resin.		
a.	. .	46·8	23·4	. .	. .	. .	2·1	26·6	. .	. .	. .	=	98·9
b.	. .	44·0	26·5	8·0	. .	0·5	. .	20·5	. .	. .	. .	=	99·5
c.	. .	23·3	16·1	10·3	3·1	1·1	3·1	43·0	. .	. .	. .	=	100·
d.	0·55	46·44	17·40	6·22	0·09	0·86	1·25	12·69	6·95	6·46	0·56	=	99·47

Ferric Silicates. There are but few ferric silicates of definite composition. Degeroïte, from Finland (ii. 309), consists mainly of $Fe^2O^3.SiO^2.3aq$.—Anthosiderite, from Minas Geraes, Brazil (i. 309), is $2Fe^2O^3.9SiO^2.2aq$.—Chloropal (i. 921) is a mixture of $Fe^2O^3.3SiO^2.3aq$. with opal.—Pinguite (iv. 650) has nearly the composition $Fe''O.3SiO^2.4(Fe^2O^3.2SiO^2).30aq$.—Nontronite (iii. 134), unghwarite (*q. v.*), and a ferruginous bole from Halsbrücke, near Freiberg, are ferric or ferroso-ferric silicates to which no definite formula can be assigned. The last contains, according to Kersten, 46·40 per cent. silica, 3·01 alumina, 23·50 ferric oxide, and 24·50 water.

Manganic Silicates. The black silicious ores of manganese, which give off chlorine when treated with hydrochloric acid, appear to have been formed by the oxidation of manganous silicates (rhodonite, cummingtonite, bustamite), and are often mixed with the latter, so that their composition is very variable.

Analyses:—*a*, *b*, *c*. Three varieties of a black silicious manganese, from Sweden: specific gravity = 2·74—2·98.—*d*. An accompanying black substance: specific gravity = 3·207 (Bahr, J. pr. Chem. liii. 308):—

	SiO^2.	Mn^2O^3.	Fe^2O^3.	Al^2O^3.	CaO.	MgO.	H^2O.		
a.	36·20	47·91	0·70	1·11	0·60	4·43	9·43	=	100·38
b.	36·11	42·00	11·31	0·90	0·70	0·57	9·43	=	101·02
c.	34·72	42·64	10·45	1·09	0·56	0·35	9·76	=	99·57
d.	23·69	56·21	9·14	0·61	0·50	0·39	9·50	=	100·04

e. Stratopeite, a black amorphous mineral, of specific gravity 2·64, from the Pajsberg mine, near Philipstad in Sweden, containing, according to Igelström (J. pr. Chem. liv. 192, 290), 35·43 per cent. silica, 32·41 manganic oxide, 10·27 ferric oxide, 8·04 magnesia, and 13·75 water, is a decomposition-product of similar character.

f. A black silicious manganese from Klapperud, in Dalarne, Sweden, in which Klaproth found 25 per cent. silica, 55·8 manganous oxide, and 13·0 loss by ignition, was probably a hydrated mixture of manganous silicate, manganous carbonate, and manganic oxide or peroxide; the deficiency in the analysis (6 2 per cent.) was probably carbonic anhydride.

g, *h*, *i*. Marceline or Heterochine, from St. Marcel in Piedmont: *g* by Berzelius (Afhandl. i. Fis. iv. 382); *h* by Ewreinoff (Pogg. Ann. xlix. 204); *i* by Damour (J. pr. Chem. xxviii. 284).—*k*. Dense, hard, silicious manganese from Tinzen in the Grisons (Berthier, Ann. Ch. Phys. [2] li. 79).—*l*. The same by Schweizer (J. pr. Chem. xxiii. 278):—

	SiO^2.	Mn^2O^3.	Fe^2O^3.	Al^2O^3.	CaO.	MgO.	K^2O.	H^2O.		
g.	15·17	75·80	4·14	2·80	. .	. .	. .	. .	=	97·91
h.	10·16	85·87	3·28	. .	0·61	. .	0·44	. .	=	100·36
i.	10·24	76·32	11·49	. .	1·14	0·26	. .	. .	=	99·45
k.	15·3	80·9	1·0	1·0	. .	. .	. .	. .	=	98·2
l.	15·50	77·34	3·70	. .	1·70	. .	. .	1·76	=	100

g, *k*, and *l* are, approximately, $2Mn^2O^3.3SiO^2$, but they may also be mixtures; *h* and *k* are still less definite.

A brown sinter from the mine-waters of Himmelfahrt, near Freiberg, was found by

a. ANHYDROUS SILICATES.

Name.	Oxygen-ratio.		Formula.	Metals.	
	Bases : SiO^2	$\left.\begin{matrix}M^2O\\ \text{or}\\ \bar{M}''O\end{matrix}\right\}$; $\overset{'''}{R}{}^2O^3$; SiO^2		$\left.\begin{matrix}M\\ \bar{M}''\end{matrix}\right\}$	R'''
Gehlenite	1 : $\frac{2}{3}$	1 : 1 : $\frac{4}{3}$	$3\bar{M}O.R^2O^3.2SiO^2$	Ca, Mg, Fe	Al, Fe
Lievrite	1 : $\frac{4}{5}$	1 : $\frac{2}{3}$: $\frac{4}{3}$	$9\bar{M}O.2R^2O^3.6SiO^2$	Fe, Ca	Fe
Humboldtilite	1 : 1	1 : $\frac{1}{2}$: $\frac{3}{2}$	$12(M^2;\bar{M})O.2R^2O^3.9SiO^2$	Ca, Mg, Na, K	Al, Fe
Vesuvian				Ca, Mg	Al, Fe
Orthite	1 : 1	1 : 1 : 2	$3\bar{M}O.R^2O^3.3SiO^2$	Ca, Ce, La, Di, Fe, Mg	Al, Fe
Sarcolite				Ca, Na, K	Al
Garnet				Ca, Mg, Fe, Mn	Al, Fe, Cr
Epidote group	1 : 1	1 : 2 : 3	$6\bar{M}O.4R^2O^3.9SiO^3$	Ca, Mg, Fe, Mn	Al, Fe, Mn
Mejonite				Ca	Al
Anorthite	1 : 1	1 : 3 : 4	$(M^2;\bar{M})OR^2.O^3.2SiO^2$	Ca	Al
Sodalite group				Na, Ca*	Al
Nepheline (Elæolite)	1 : $1\frac{1}{8}$	1 : 3 : $4\frac{1}{2}$	$4M^2O.4R^2O^3.9SiO^2$	Na, K	Al
Dichroïte	1 : $1\frac{1}{4}$	1 : 3 : 5	$2\bar{M}O.2R^2O^3.5SiO^2$	Mg	Al, Fe
Barsowite				Ca	Al
Ersbyite	1 : $1\frac{1}{2}$	1 : 3 : 6	$(M^2;\bar{M})O.R^2O^3.3SiO^2$	Ca	Al
Labradorite				Ca, Na	Al
Babingtonite	1 : 2	1 : $\frac{1}{3}$: $2\frac{2}{3}$	$9\bar{M}O.R^2O^3.12SiO^2$	Ca, Mn, Fe	Fe
Beryll	1 : 2	1 : 1 : 4	$3(M^2;\bar{M})O.R^2O^3.6SiO^2$	G	Al
Aegirin				Fe, Ca, Na	Fe
Arfvedsonite	1 : 2	1 : $1\frac{1}{2}$: 5	$2(M^2;\bar{M})O.R^2O^3.5SiO^2$	Fe, Na	Fe
Achmite	1 : 2	1 : 2 : 6	$3(M^2;\bar{M})O.2R^2O^3.9SiO^2$	Na, Fe	Fe
Leucite	1 : 2	1 : 3 : 8	$(M^2;\bar{M})O.R^2O^3.4SiO^3$	K	Al
Hyalophane				Ba, K	Al
Andesin				Ca, Na	Al
Spodumene	1 : 2	1 : 4 : 10	$3M^2O.4R^2O^3.15SiO^2$	Li, Na	Al
Oligoclase	1 : $2\frac{1}{2}$	1 : 3 : 9	$2(M^2;\bar{M})O.2R^2O^3.9SiO^2$	Ca, Na, K	Al
Orthoclase	1 : 3	1 : 3 : 12	$M^2O.R^2O^3.6SiO^2$	K, Na	Al
Albite				Na, K	Al
Petalite (Castor)	1 : 4	1 : 4 : 20	$3M^2O.4R^2O^3.30SiO^2$	Li, Na	Al

* With NaCl and sulphates.

B. Hydrated Silicates.

Name.	Oxygen-ratio.		Formula.	Metals.	
	Bases : $\mathrm{SiO^2}$	$\left.\begin{matrix}\mathrm{M^2O}\\ \mathrm{\bar{M}O}\end{matrix}\right\}$: $\mathrm{R^2O^3 : SiO^2 : H^2O}$		$\left.\begin{matrix}\mathrm{M}\\ \mathrm{\bar{M}''}\end{matrix}\right\}$	R'''
Chloritoïd	$1 : \frac{1}{2}$	$1 : 3 : 2 : 1$	$\mathrm{\bar{M}O.R^2O^3.SiO^2.aq.}$	Fe, Mg	Al, Fe
Margarite	$1 : \frac{4}{7}$	$1 : 6 : 4 : 1$	$\mathrm{(M^2;\bar{M})O.2R^2O^3.2SiO^2.aq.}$	Ca, K	Al, Fe
Thuringite	$1 : \frac{3}{5}$	$1 : 1\frac{1}{2} : 1\frac{1}{2} : 1$	$\mathrm{4\bar{M}O.2R^2O^3.3SiO^2.4aq.}$	Fe, Mg	Al, Fe
Euclase	$1 : \frac{4}{5}$	$1 : 1\frac{1}{2} : 2 : \frac{1}{2}$	$\mathrm{2\bar{M}O.R^2O^3.2SiO^2.3aq.}$	G	Al
Chlorastrolite	$1 : 1$	$1 : 2 : 3 : 1$	$\mathrm{6(M^2;\bar{M})O.4R^2O^3.9SiO^2.6aq.}$	Ca, Na	Al, Fe
Thomsonite	$1 : 1$	$1 : 3 : 4 : 2\frac{1}{2}$	$\mathrm{2[(M^2;\bar{M})O.R^2O^3.2SiO^2].5aq.}$	Ca, Na	Al
Gismondin	$1 : 1$	$1 : 3 : 4 : 4$	$\mathrm{(M^2;\bar{M})O.R^2O^3.2SiO^2.4aq.}$	Ca, K	Al
		$[1 : 3 : 4\frac{1}{2} : 4\frac{1}{2}]$?			
Damourite	$1 : 1\frac{1}{5}$	$1 : 9 : 12 : 2$	$\mathrm{\bar{M}O.3R^2O^3.6SiO^2.2aq.}$	Ca	Al
		$[1 : 9 : 11 : 2]$?			
Groppite	$1 : 1\frac{1}{5}$	$1 : 1\frac{1}{2} : 3 : 1$	$\mathrm{2M^2O.R^2O^3.3SiO^2\,2aq.}$	K	Al
Prehnite	$1 : 1\frac{1}{5}$	$1 : 1\frac{1}{2} : 3 : \frac{1}{2}$	$\mathrm{2(M^2;\bar{M})O.R^2O^3.3SiO^2.aq.}$	Mg, Ca, K	Al, Fe
Hydrates of Dichroïte Esmarkite, Fahlunite, Chlorophyllite), &c.	$1 : 1\frac{1}{4}$	$1 : 3 : 5 : n$	$\mathrm{2\bar{M}O.2R^2O^3.5SiO^2.}n\,\mathrm{aq.}$	Mg	Al, Fe
Brevicite	$1 : 1\frac{1}{4}$	$1 : 3 : 5 : 2$	$\mathrm{2(M^2;\bar{M})O.2R^2O^3.5SiO^2.4aq.}$	Na, Ca	Al
Färolite	$1 : 1\frac{1}{4}$	$1 : 3 : 5 : 2\frac{1}{2}$	$\mathrm{2[2(M^2;\bar{M})O.2R^2O^3.5SiO^2].5aq.}$	Ca, Na	Al
Mesotype	$1 : 1\frac{1}{2}$	$1 : 3 : 6 : 2$	$\mathrm{M^2O.R^2O^3.3SiO^2.2aq.}$	Na	Al
Mesolite	$1 : 1\frac{1}{2}$	$1 : 3 : 6 : 3$	$\mathrm{(M^2;\bar{M})O.R^2O^3.3SiO^2.3aq.}$	Ca, Na	Al
Scolecite			$\mathrm{\bar{M}O.R^2O^3.3SiO^2.3aq.}$	Ca	Al
Zeagonite	$1 : 1\frac{1}{2}$	$1 : 3 : 6 : 4$	$\mathrm{(M^2;\bar{M})O.R^2O^3.3SiO^2.4aq.}$	Ca, K	Al
Levyne				Ca, Na, K	Al
Analcime	$1 : 2$	$1 : 3 : 8 : 6$	$\mathrm{M^2O.R^2O^3.4SiO^2.6aq.}$	Na	Al
Leonhardite	$1 : 2$	$1 : 3 : 8 : 3$	$\mathrm{\bar{M}O.R^2O^3.4SiO^2.3aq.}$	Ca	Al
		$[1 : 4 : 10 : 5]$?			
Laumontite	$1 : 2$	$1 : 3 : 8 : 4$	$\mathrm{\bar{M}O.R^2O^3.4SiO^2.4aq.}$	Ca	Al
Herschelite	$1 : 2$	$1 : 3 : 8 : 5$	$\mathrm{(M^2;\bar{M})O.R^2O^3.4SiO^2.5aq.}$	Na, K, Ca	Al
Phillipsite				Ca, K, Na	Al
Gmelinite	$1 : 2$	$1 : 3 : 8 : 6$	$\mathrm{(M^2;\bar{M})O.R^2O^3.4SiO^2.6aq.}$	Na, Ca	Al
Chabasite (A)			$\mathrm{\bar{M}O.R^2O^3.4SiO^2.6aq.}$	Ca	Al
Chabasite (B)	$1 : 2\frac{1}{4}$	$1 : 3 : 9 : 6$	$\mathrm{2\bar{M}O.2R^2O^3.9SiO^2.12aq.}$	Ca	Al
Faujasite	$1 : 2\frac{1}{4}$	$1 : 3 : 9 : 9$	$\mathrm{2(M^2;\bar{M})O.2R^2O^3.9SiO^2.18aq.}$	Ca, Na	Al
Harmotome	$1 : 2\frac{1}{2}$	$1 : 3 : 10 : 5$	$\mathrm{(M^2;\bar{M})O.R^2O^3.5SiO^2.5aq.}$	Ba, K	Al
Parastilbite	$1 : 3$	$1 : 3 : 12 : 3$	$\mathrm{(M^2;\bar{M})O.R^2O^3.6SiO^2.3aq.}$	Ca, Na, K	Al
Brewsterite	$1 : 3$	$1 : 3 : 12 : 5$	$\mathrm{(M^2;\bar{M})O.R^2O^3.6SiO^2.5aq.}$	Sr, Ba	Al
Epistilbite				Ca, Na	Al
Stilbite (Heulandite)				Ca, Na	Al
Desmin (Stilbite)	$1 : 3$	$1 : 3 : 12 : 6$	$\mathrm{(M^2;\bar{M})O.R^2O^3.6SiO^2.6aq.}$	Ca, Na	Al

Kersten to contain 18·98 per cent. silica, 25·01 manganic oxide, 22·90 ferric oxide, and 33·00 water, which may be represented by the formula $\mathrm{(Mn^2O^3;Fe^2O^3).3SiO^2.6aq}$.

Carpholite (p. 257) is a manganic silicate containing alumina and ferric oxide.

Silicates containing Monatomic, Diatomic, and Triatomic Metals: Double Silicates.

These compounds being specially described, and their analyses given in separate articles, it will be sufficient to give in this place a tabular view of the composition of those whose formulæ may be considered as definitely established. In the preceding tables (pp. 260, 261), to avoid the continual repetition of atomicity-marks, a monatomic metal is denoted by M, a diatomic metal by $\bar{\mathrm{M}}$, and a triatomic metal by R.

Compounds or Mixtures of Silicates with other Salts.

1. With *Aluminates.*—It has already been mentioned (p. 253), that certain varieties of augite and hornblende may be regarded as mixtures of silicates and aluminates of magnesia, &c. A similar composition is also assigned to the following minerals, the alumina being more or less replaced by ferric oxide:

Clintonite, $\mathrm{(2\bar{M}O.3SiO^2)\,.\,2(3\bar{M}O\,.\,2Al^2O^3)}$.
Xanthophyllite, $\mathrm{(\bar{M}O.3SiO^2)\,.\,3(3\bar{M}O.2Al^2O^3)\,.\,3aq}$.
Disterrite or Brandisite $\mathrm{(2\bar{M}O.3SiO^2)\,.\,4(\bar{M}O.Al^2O^3)\,.\,2aq}$.

The minerals of the **chlorite** group may be represented either as double silicates of magnesia (ferrous oxide) and alumina, or as compounds of silicates and aluminates: thus—

Chlorite, $\mathrm{6\bar{M}O.Al^2O^3.3SiO^2.4aq.} = \mathrm{2(3\bar{M}O.SiO^2)\,.\,(Al^2O^3.SiO^2)\,.\,4aq}$.
$= \mathrm{(4\bar{M}O.3SiO^2)\,.\,(2MO.Al^2O^3)\,.\,4aq}$.
Ripidolite, $\mathrm{4\bar{M}O.Al^2O^3.2SiO^2.3aq.} = \mathrm{(4\bar{M}O.SiO^2)\,.\,(Al^2O^3.SiO^2)\,.\,3aq}$.
$= \mathrm{4(\bar{M}O.SiO^2)\,.\,(3MO.Al^2O^3)\,.\,3aq}$.

2. With *Borates.*—The native calcic borosilicates have already been mentioned, viz.:—

Datholite, $\mathrm{CaB^2O^4.CaSiO^3.aq}$.
Botryolite, $\mathrm{CaB^2O^4.CaSiO^3.2aq}$.

Tourmalines are double silicates, containing both proto- and sesquioxides, most of which may be included in the general formula,

$$\mathrm{2(M^2;\bar{M})O.SiO^2\,.\,}n\mathrm{(R;B)^2O^3.SiO^2},$$

the boron being supposed to replace a portion of the triatomic metal R.

Axinite is a borosilicate containing

$$\mathrm{3[2CaO.SiO^2]\,.\,2[(R;B)^2O^3.3SiO^2]}.$$

3. With *Carbonates.*—**Cancrinite** consists of $\mathrm{(CaO.CO^2).3[Na^2O.Al^2O^3.2SiO^2]}$, or $\mathrm{CaCO^3.3(Na^2SiO^3.Al^2SiO^5)}$.

4. With *Chlorides.*—**Sodalite** consists of a sodio-aluminic silicate combined with chloride of sodium, and may be represented by the formula $\mathrm{NaCl.}n\mathrm{(Na^4SiO^4.Al^4Si^3O^{12})}$. **Porcelain-spar** contains, according to Schafhäutl, a small quantity of potassic chloride.

5. With *Fluorides.*—**Lepidolite** consists of 6 or 12 at. of a silicate of aluminium and alkali-metals, including lithium, with 1 at. of a fluoride; or the fluorine may be regarded as replacing a portion of the oxygen in the silica. (For the formula, see iii. 1011). A similar replacement of oxygen by fluorine takes place to a small extent in many other silicates.

6. With *Sulphates.*—This division includes **haüyne**, **nosean**, **ittnerite**, and **ultramarine**. The composition of the first three is as follows:—

Haüyne, $\mathrm{(M^2;\bar{M})SO^4} + n\mathrm{[(M^2;\bar{M})SiO^3.Al^2SiO^5]}$.
Nosean, $\mathrm{NaCl} + \mathrm{3(Na^2SiO^3.Al^2SiO^5)}$
$+ \mathrm{10[Na^2SO^4.3(Na^2SiO^3.Al^2SiO^5)]}$.
Ittnerite, $\mathrm{NaCl} + \mathrm{3[Na^2SiO^3.Al^2SiO^5).6aq}$.
$+ \mathrm{3[(Ca;Na^2)SO^4.3[(Ca;Na^2)SiO^3.Al^2SiO^5].6aq}$.

Nosean is a compound of 1 at. sodalite and 10 at. of a soda-haüyne; ittnerite of 1 at. hydrated sodalite and 3 at. of a hydrated haüyne. Lapis-lazuli, or ultramarine, is a mixture of variable composition.

7. With *Titanates.*—The following minerals of this class are known:—

Titanite, $\mathrm{Ca''^2}\left\{\begin{matrix}\mathrm{SiO^3}\\ \mathrm{TiO^3}\end{matrix}\right. = \mathrm{Ca''SiO^3.Ca''TiO^3}$.

Yttrotitanite, $\mathrm{\bar{M}^3R^8O^{15}.15\bar{M}(Si;Ti)^2O^5}$; $\mathrm{[\bar{M} = Ca, Y;\ R = Al, Fe]}$.

Schorlamite, $9Ca''\begin{cases}\tfrac{3}{5}SiO^3\\ \tfrac{2}{5}TiO^3\end{cases} + \overset{'''}{Fe^2}\begin{cases}\tfrac{3}{5}Si^3O^9\\ \tfrac{2}{5}Ti^3O^9\end{cases}$.
Tschewkinite, $Fe''(Si;Ti)^{iv}O^3 . 3(Ca;La;Di;Ca)''.(Si;Ti)^{iv}O^3$.
Enceladite, $6(Mg;Fe;Ca)^7(Si;Ti)O^4 . Al^4(Si;Ti)^9O^{12}.6aq$.

Mosandrite is a hydrated silicotitanate, containing cerium, lanthanum, didymium, iron, calcium, magnesium, potassium, and sodium; but its exact composition has not been determined.

8. With *Tungstates.*—There are no native minerals consisting of silicates and tungstates; but Marignac has lately obtained a series of such compounds artificially. (See TUNGSTATES.)

9. With *Zirconates.*—**Eudialyte**, from Greenland, consists of $(Na^2;Ca'';Fe'')(Si;Zr)^{iv}O^3$; Norwegian eudialyte contains the same elements, but in somewhat different proportions.

Catapleiite, from the syenite of Lamö, near Brevig in Norway, consists of $(Na^2;Ca'';Fe'')(Si^{iv};Zr^{iv})^4O^9.2aq.$ or $(Na^2;Ca;Fe'')(Si;Zr)^{iv}O^3.3(Si;Zr)^{iv}O^2.2aq$.

Oerstedite is a hydrated silico-zirconio-titanate of calcium, magnesium, and iron, the formula of which has not been exactly determined.

10. With *Zirconates* and *Niobates.*—**Wöhlerite**, from the Langesundfjord, near Brevig in Norway, probably consists of $(Ca'';Na^2)(Si;Zr.Nb)^{iv}O^3$. In the same neighbourhood is found a red-brown mineral of similar character, but containing no zirconium, probably formed by alteration of the wöhlerite.

SILICIC ETHERS. (Ebelmen, Ann. Ch. Phys. [3] xvi. 144.—Friedel and Crafts, Ann. Ch. Phys. [4] ix. 5.)—Silicates of alcohol-radicles produced by the action of alcohols on silicic chloride.

Amylsilicic Ethers. *Tetramylic Silicate*, $(C^5H^{11})^4SiO^4 = 2(C^5H^{11})^2O.SiO^2$.—Prepared like the corresponding ethyl-compound, the product, which passes over between 320° and 340°, being collected apart and rectified. It is a colourless limpid liquid, having a faint odour, somewhat like that of amylic alcohol. Specific gravity = 0·868 at 20°. Boiling-point between 322° and 325°. Vapour-density: obs. = 15·2; calc. = 13·03. It burns with a long white flame, depositing impalpable silica. It dissolves freely in ethylic alcohol, ethylic ether, and amylic alcohol, is insoluble in water, and is decomposed thereby much less quickly than the ethylic silicates. Alcoholic ammonia also decomposes it with difficulty. (Ebelmen.)

Ethylsilicic Ethers. *Tetrethylic Silicate*, $(C^2H^5)^4SiO^4 = 2(C^2H^5)^2O.SiO^2$.—When a small quantity of absolute alcohol is poured upon silicic chloride, a brisk action takes place, accompanied by copious evolution of hydrochloric acid, and a considerable depression of temperature; and on distilling the resulting transparent and colourless liquid, more hydrochloric acid is evolved, then towards 90° a strongly acid product, after which the temperature quickly rises to 160°, at which point tetrethylic silicate passes over, and must be collected in a separate receiver.

Tetrethylic silicate is a colourless liquid, having a rather pleasant ethereal odour, and a strong peppery taste. Specific gravity = 0·933 at 20° (Ebelmen); 0·9676 (Friedel and Crafts). It boils without alteration between 165° and 166°. Vapour-density: obs. = 7·32; calc. = 7·207. It is combustible and burns with a dazzling flame, diffusing a white smoke, consisting of silica in a state of extremely minute division. It is insoluble in water, which however decomposes it gradually, with separation of gelatinous silica. Ammonia and the fixed alkalis dissolve and decompose it with facility. (Ebelmen.)

According to Knop and Wolf (Jahresb. 1861, p. 207), the liquid obtained by saturating absolute alcohol (kept cool) with fluoride of silicon, is a mixture of tetrethylic silicate and silicofluoric acid (p. 270).

Diethylic Silicate, $(C^2H^5)^2SiO^3 = (C^2H^5)^2O.SiO^2$, is produced by the action of silicic chloride on aqueous alcohol:

$$SiCl^4 + 2C^2H^6O + H^2O = (C^2H^5)^2SiO^3 + 4HCl.$$

It is a colourless liquid, having a faint odour, specific gravity = 1·079, and boiling at 350°. Water decomposes it with separation of silica. When it is left in contact with moist air, the silica solidifies to a transparent mass, which contracts more and more, and acquires in two or three months the lustre and vitreous fracture of hyaline quartz, and becomes hard enough to scratch glass. (Ebelmen.)

Diethylic Disilicate, $(C^2H^5)^2Si^2O^5 = (C^2H^5)^2O.2SiO^2$, is formed by distilling the preceding compound with a small quantity of aqueous alcohol. Diethylic silicate then passes over first, and diethylic disilicate remains in the retort. If, however, too much heat is applied, more diethylic silicate is given off, and free silica remains behind. (Ebelmen.)

Diethylic disilicate dissolves in ether, alcohol, and the other silicic ethers.

Hexethylic Disilicate, $(C^2H^5)^6Si^2O^7 = 3(C^2H^5)^2O.2SiO^2$.—Friedel and Crafts were not able to obtain the two ethylic silicates last mentioned; but having prepared a considerable quantity of ethylic silicate with alcohol that was not quite anhydrous, they found that the greater part of the product distilled over towards 240°, but that it was not possible, by distillation under the ordinary atmospheric pressure, to obtain a product of definite boiling-point. By distillation *in vacuo*, however (under a pressure of 3 to 5 mm.) they obtained, after eight fractionations, a product boiling between 125° and 130°, and having the composition of hexethylic disilicate.

This ether is a slightly oily liquid, having a rather fragrant odour like that of normal silicic ether. Specific gravity of 1·0196 at 0°, and 1·0119 at 19°. Vapour-density: obs. = 12·025; calc. = 11·86.

Ethylsilicic Chlorhydrins.—By heating chloride of silicon with tetrethylic silicate in various proportions, Friedel and Crafts have obtained compounds derived from the latter by substitution of 1, 2, and 3 at. chlorine for an equivalent quantity of hydroxyl (HO).

Ethylsilicic monochlorhydrin, $(C^2H^5)^3ClSiO^3$, is produced: 1. By heating 1 at. silicic chloride with 3 at. tetrethylic silicate to 150° for an hour in a closed vessel:

$$SiCl^4 + 3(C^2H^5)^4SiO^4 = 4(C^2H^5)^3ClSiO^3.$$

2. Together with ethylic acetate, by heating 1 at. tetrethylic silicate with 1 at. chloride of acetyl to 170°—180°:

$$(C^2H^5)^4SiO^4 + C^2H^3OCl = (C^2H^5)^3ClSiO^3 + (C^2H^3O)(C^2H^5)O^2.$$

3. By distilling tetrethylic silicate with pentachloride of phosphorus. It is a limpid liquid, of specific gravity 1·0483 at 0°. Boils at 157°. Vapour-density: obs. = 7·05; calc. = 6·81. It does not fume in the air, but is quickly decomposed by the action of moist air and of water, yielding hydrochloric acid and silica. It burns with a green-edged flame, diffusing white fumes of silica.

Ethylsilicic Dichlorhydrin, $(C^2H^5)^2Cl^2SiO^2$.—Produced by heating 1 at. tetrethylic silicate with 1 at. silicic chloride:

$$SiCl^4 + (C^2H^5)^4SiO^4 = 2(C^2H^5)^2Cl^2SiO^2;$$

or 1 at. silicic chloride with 2 at. of the monochlorhydrin:

$$SiCl^4 + 2(C^2H^5)^3ClSiO^3 = 3(C^2H^5)^2Cl^2SiO^2.$$

In either case the materials must be heated together for some time, and the product purified by repeated fractional distillation, great care being taken to prevent access of moisture. It is a liquid resembling the preceding, and having a specific gravity of 1·44 at 0°. Boiling-point 137°. Vapour-density: obs. = 6·76; calc. = 6·545.

Ethylsilicic Trichlorhydrin, $(C^2H^5)Cl^3SiO$.—Prepared by heating the dichlorhydrin, monochlorhydrin, or tetrethylic silicate, for a long time with excess of silicic chloride, and fractionating the product a great number of times with the precautions above indicated. It is a liquid of specific gravity 1·291 at 0°, boiling at 104°. Vapour-density: obs. = 6·378; calc. = 6·216.

Ethylamylic Silicates.—These ethers are produced by distilling ethylsilicic mono-, di-, or tri-chlorhydrin with an equivalent quantity of amylic alcohol: *e. g.*—

$$\underset{\substack{\text{Ethylsilicic}\\ \text{monochlorhydrin.}}}{(C^2H^5)^3ClSiO^3} + \underset{\substack{\text{Amylic}\\ \text{alcohol.}}}{(C^5H^{11})HO} = \underset{\substack{\text{Amyl-triethylic}\\ \text{silicate.}}}{(C^2H^5)^3(C^5H^{11})SiO^4} + HCl.$$

The *monamylic compound*, $(C^2H^5)^3(C^5H^{11})SiO^4$, is a limpid slightly oily liquid, having a faint odour, like that of amyl-compounds in general; boils between 216° and 225°.—The *diamylic compound*, $(C^2H^5)^2(C^5H^{11})^2SiO^4$, has a specific gravity of 0·915 at 0°, and boils between 245° and 250°.—The *triamylic compound*, $(C^2H^5)(C^5H^{11})^3SiO^4$, has a specific gravity of 0·913 at 0°, and boils between 280° and 285°. These mixed ethers, like tetramylic silicate, are less easily decomposed by alcoholic ammonia than tetrethylic silicate. (Friedel and Crafts.)

Triethyl-acetylsilicic Ether, $(C^2H^5)^3(C^2H^3O)SiO^4$. *Ethylic Silico-acetin.*—Produced by heating tetrethylic silicate with acetic anhydride to 180° for fourteen hours, and separated by fractional distillation. It is a limpid slightly oily liquid, with a slightly acetic odour, becoming stronger after exposure for some time to a moist atmosphere. Boils at about 190°. Burns with emission of white clouds of silica.

Methylsilicic Ethers. (Friedel and Crafts, Ann. Ch. Phys. [4] ix. 32.)—*Tetramethylic silicate*, $(CH^3)^4SiO^4$, is prepared, like the corresponding ethyl-compound, by the action of silicic chloride on perfectly pure and anhydrous methylic alcohol (obtained by distilling ordinary methylic alcohol, first over sodium, and then over phosphoric anhydride). It is a colourless limpid liquid, having a fragrant ethereal odour, and a specific gravity of 1·0589 at 0°. Boils at 121°—122°. Vapour-density: obs. = 5·380; calc. = 5·264. It is moderately soluble in water, the solution remaining clear, and not depositing gelatinous silica till after the lapse of several weeks. It burns with emission of white fumes. It is rapidly decomposed by exposure to moist air. Aqueous alcohol converts it into a mixture of methylic polysilicates.

Hexmethylic Disilicate, $(CH^3)^6Si^2O^7 = 3(CH^3)^2O.2SiO^2$, is obtained in the preparation of tetramethylic silicate when the methyl-alcohol used is not quite anhydrous: also by heating the tetramethylic ether with wood-spirit containing the quantity of water required by theory for its production: $2(CH^3)^4SiO^4 + H^2O = (CH^3)^6Si^2O^7 + 2(CH^3)HO$. It resembles the tetramethylic ether, has a specific gravity of 1·1441 at 0°, and boils between 201° and 202·5. Vapour-density: obs. = 9·19; calc. = 8·93.

Methylsilicic Chlorhydrins.—These compounds are precisely analogous to the ethylsilicic chlorhydrins already described, and are obtained in like manner. They are limpid liquids, having an ethereal odour, burning with a green-edged flame, and diffusing white clouds of silica; easily decomposed by moisture; converted by wood-spirit into tetramethylic silicate. Their densities and boiling-points are exhibited in the following table:—

	Boiling-point.	Specific gravity at 0°.	Vapour-density.	
			obs.	calc.
Monochlorhydrin, $(CH^3)^3ClSiO^3$.	114·5°—115·0°	1·1954	5·578	5·42
Dichlorhydrin, $(CH^3)^2Cl^2SiO^2$ . .	98° —103°	1·2595	5·66	5·57
Trichlorhydrin, $(CH^3)Cl^3SiO$ . . .	82° —86°		5·66	5·73

Methyl-ethylsilicic Ethers.—These compounds are produced by the action of ethylic alcohol on the methylsilicic chlorhydrins.

Ethyl-trimethylic Silicate, $(CH^3)^3(C^2H^5)SiO^4$, is obtained, together with a small quantity of the following compound, by treating methylsilicic monochlorhydrin with excess of common alcohol. It boils between 133° and 135°.

Diethyl-dimethylic Silicate, $(CH^3)^2(C^2H^5)^2SiO^4$, is obtained by the action of ethylic alcohol on methylsilicic dichlorhydrin, and by that of methylic alcohol on tetrethylic silicate. It is a liquid of specific gravity 1·004 at 0°, and boiling between 143° and 146°. Vapour-density: obs. = 6·178; calc. = 6·233.

Triethyl-methylic Silicate, $(CH^3)(C^2H^5)^3SiO^4$, is obtained by the action of ethylsilicic monochlorhydrin on methylic alcohol. It has a specific gravity of 0·981 at 0°, and boils between 155° and 157°.

Dimethyl-diamylic Silicate, $(CH^3)^2(C^5H^{11})^2SiO^4$.—Produced by distilling methylsilicic monochlorhydrin with two-thirds of its weight of amylic alcohol. Boils between 225° and 235°. Decomposed by alcoholic potash, but not easily by alcoholic ammonia.

SILICIDES, METALLIC. Silicon unites readily with aluminium, iron, zinc, platinum, and some other metals, but not with sodium, and apparently not with lead or potassium. Towards aluminium and zinc, silicon behaves in the same manner as carbon to cast-iron, dissolving in these metals when melted, and separating in the crystalline form on cooling.

Silicide of Calcium, probably $CaSi^2$, is prepared by intimately mixing 300 grains of graphitoïdal silicon with 3,000 grains of chloride of calcium in a hot mortar, briskly agitating the mixture in a wide-mouthed bottle with 350 grains of sodium cut into small pieces, and introducing the whole into a red-hot crucible, into which a little fused common salt has been previously thrown, and upon this a mass of sodium weighing 350 grains. The whole is then covered with a layer of fused and pulverised chloride of sodium, the cover is put on, and the fire is gradually raised to a temperature sufficient to melt cast-iron, at which it must be maintained for half an hour. On breaking the crucible when cold, the silicide of calcium is found (if the operation has been successful) in a well-fused button, which must be preserved in tightly-closed vessels.

Silicide of calcium has a lead-grey colour, metallic lustre, and scaly crystalline structure with an indistinct indication of hexagonal plates. When exposed to the air, or thrown into water, it slowly crumbles down to a mass of graphite-like plates, with evolution of hydrogen. This disintegration is due to the hydration and oxidation of part of the calcium and silicon, the new products remaining mixed with some unaltered silicide. Fuming nitric acid does not attack silicide of calcium. Hydrochloric, acetic, or dilute sulphuric acid converts it into a compound of silicon, hydrogen, and oxygen, called silicone or chryseone (p. 275).—(Wöhler, Ann. Ch. Pharm. cxxvii. 257.)

Silicide of Cerium, CeSi.—When a mixture of fluoride of potassium and oxide of cerium, fused in a porcelain crucible, is subjected to electrolysis, silicide of cerium is deposited at the negative pole together with potassium; and on washing the deposit with water to remove the latter, the silicide of cerium remains as a brown powder, which is insoluble in acids, and burns with a reddish flame, leaving a yellow powder mixed with black particles. (Ulik, Zeitschr. f. Chem. [2] ii. 60.)

Silicides of Copper.—These compounds possess great hardness, and become harder but less malleable as the proportion of silicon increases. A white copper-silicide, very hard to the file, is formed in the preparation of silicon by passing the vapour of silicic chloride over sodium heated in copper trays. A copper silicide containing 12 pts. silicon to 88 pts. copper is obtained by fusing 3 pts. of potassic silicofluoride, 1 pt. sodium, and 1 pt. copper-turnings, at such a temperature that the melted metal is covered by a very fluid slag. The compound is white, brittle, and more fusible than silver. By fusing this silicide with a larger quantity of copper, a compound may be obtained containing 4·8 per cent. silicon: it has a fine light bronze colour, is as malleable as ordinary bronze, somewhat less hard than iron, and may be wrought like the latter, is very malleable, and may be drawn out into wire having at least as much tenacity as iron wire. (Deville and Caron, Ann. Ch. Pharm. civ. 232; Ann. Ch. Phys. [3] lxvii. 455.)

By precipitating cupric sulphate with siliciuretted hydrogen, a copper-silicide is obtained, as a dark copper-coloured film, translucent with brownish colour when very thin. This compound is easily oxidisable, being quickly converted, by exposure to the air at ordinary temperatures, into lemon-yellow cupric silicate. Dilute nitric acid decomposes it immediately, separating metallic copper; hydrochloric acid dissolves it, with evolution of hydrogen and separation of silicic oxide. With potash-ley it quickly gives off hydrogen, and deposits copper free from silicon; it also gives off hydrogen in contact with ammonia.

Silicide of Iron. See IRON (iii. 334).

Silicide of Magnesium.—The mass obtained by fusing together chloride of magnesium, chloride of sodium, silicofluoride of sodium, and metallic sodium, for the preparation of siliciuretted hydrogen, contains, besides free silicon, two silicides of magnesium, one of which gives off siliciuretted hydrogen when treated with aqueous sal-ammoniac or hydrochloric acid; whereas the other, when treated with hydrochloric acid, yields free hydrogen and hydrated oxide of silicon. (Wöhler).

Silicide of Manganese. See MANGANESE (iii. 816).

Silicide of Platinum.—Platinum unites readily with silicon, forming a very fusible compound: hence, on fusing silicon in a platinum crucible lined with lime, care must be taken to make the lining very dense, as, if the silicon comes in contact with the platinum, the crucible will be perforated.

Silicide of Potassium(?).—According to Berzelius, silicide of potassium is formed in the preparation of silicon by heating potassic silicofluoride with potassium; but, according to Deville, the potassium is merely mixed with the free silicon.

SILICIDES, ORGANIC. (Friedel and Crafts, Bull. Soc. Chim. 1863, p. 468; 1865, i. 358.)—*Silicon-ethyl*, *ethylic silicide*, or *silicic ethide*, $Si(C^2H^5)^4$, and the corresponding *methyl-compound*, $Si(CH^3)^4$, are prepared by heating silicic chloride with zinc-ethyl and zinc-methyl respectively in sealed tubes. They are limpid liquids lighter than water, and burning with a bright flame, emitting white clouds of silica. They are not attacked by potash or by ordinary nitric acid, but are decomposed, the methyl-compound with great difficulty, by heating with fuming nitric acid in sealed tubes. Their boiling-points and vapour-densities are as follows:—

	Boiling-points.	Vapour-density.	
		Obs.	Calc.
$Si(CH^3)^4$	30°— 31°	3·083	3·043
$Si(C^2H^5)^4$	152°—154°	5·13	4·99

SILICIUM. Syn. with SILICON.

SILICO-ALUMINATES.
SILICO-BORATES. } See SILICATES (p. 262).

SILICOFLUORIDES. See SILICON, FLUORIDE OF (p. 270).

SILICON, or SILICIUM. *Atomic weight*, 28; *Symbol*, Si.—This element, though very abundant in nature, is never found in the free state, but always in combination, either with oxygen alone, as silica (p. 240), or with oxygen and metals, forming silicates.

Silicon is obtained in the free state by the action of reducing agents on the chloride or fluoride, and, like boron, assumes the amorphous, graphitoïdal, or crystalline state, according to the mode of separation adopted.

1. *Amorphous Silicon.*—This is the form in which silicon was first isolated by Berzelius (in 1823). It is obtained by heating dry potassic silicofluoride in a glass or iron tube, with eight or nine-tenths of its weight of potassium, or sodic silicofluoride with half its weight of sodium. Fluoride of potassium or sodium is then formed, and silicon is set free:

$$2KF.SiF^4 + 2K^2 = 6KF + Si.$$

The mass when cold is treated with cold water as long as the wash-water exhibits any alkaline reaction, then with boiling water as long as anything is dissolved. Silicon may also be prepared by passing the vapour of silicic chloride over potassium or sodium heated in procelain trays in a glass tube, which it is best to protect by lining it with thin plates of mica.—Amorphous silicon is likewise obtained by electrolysing a fused mixture of silicofluoride and fluoride of potassium; it may be purified from potassium deposited at the same time by washing with sulphuric acid. (Ulik.)

Silicon thus obtained is a dull brown powder, heavier than water, and insoluble therein. It is a non-conductor of electricity; soils the fingers when touched; is not acted upon by nitric or sulphuric acid, but dissolves easily in hydrofluoric acid and in warm aqueous potash. When heated in a non-oxidising atmosphere to a temperature between the melting-points of steel and cast-iron, it fuses; but when heated in air or oxygen-gas, it burns brilliantly, and is converted into silica, which melts from the intense heat, and forms a superficial crust over the unburnt silicon.

2. *Graphitoïdal Silicon.*—When amorphous silicon is strongly heated in a platinum crucible, it shrinks together, becomes much denser and darker in colour, and much less oxidisable (Berzelius). A similar modification of silicon was obtained by Deville in preparing aluminium by the electrolysis of sodio-aluminic chloride (i. 152). The first portions of aluminium thus obtained are contaminated with silicon derived from the charcoal electrodes; and when this alloy of silicon and aluminium is treated with hydrochloric acid, the silicon remains undissolved in the form of shining metallic scales resembling graphite. A more productive method of obtaining this variety of silicon is given by Wöhler (Compt. rend. xlii. 48). It consists in mixing aluminium with between 20 and 40 times its weight of silicofluoride of potassium, and heating the mixture in a Hessian crucible to the melting-point of silver. A metallic button is thus obtained, which, when treated successively with hydrochloric and hydrofluoric acids, yields graphitoïdal silicon, partly in isolated hexagonal tables, the edges of which are often curved. Another mode of preparation is to fuse 1 pt. of aluminium with 5 pts. of glass free from lead, and 10 pts. of powdered cryolite, and treat the mass first with hydrochloric, then with hydrofluoric acid. Graphitoïdal silicon exhibits all the properties ascribed by Berzelius to silicon which has been strongly heated. Its density is 2·49, which is less than that of quartz (from 2·6 to 2·8). It may be heated to whiteness in oxygen-gas without burning or undergoing any alteration in weight; but when heated to redness with *carbonate of potassium*, it decomposes the carbonic acid, with vivid emission of light and formation of silica. With *nitrate* or *chlorate of potassium*, it may be fused at a red heat without alteration, but at a white heat it burns brilliantly; the oxidation is greatly facilitated by the addition of a little carbonate of potassium. It is not attacked by any acid, excepting a mixture of nitric and hydrofluoric acids. A strong solution of *potash* or *soda* dissolves it slowly, with evolution of hydrogen. Heated to commencing redness in dry *chlorine gas*, it burns completely and forms chloride of silicon.

3. *Crystalline or Adamantine Silicon.*—α. When silicon is heated in a platinum crucible lined with lime, to a temperature between the melting-points of steel and cast-iron, it melts to dark steel-grey globules, which frequently show well-marked signs of crystallisation, and sometimes yield the silicon in double six-sided pyramids. (Deville, Ann. Ch. Phys. [3] xlix. 68.)

β. When vapour of silicic chloride is passed over aluminium kept in a state of fusion in an atmosphere of hydrogen, part of the aluminium is converted into chloride, which volatilises, and the silicon thereby separated dissolves in the remaining aluminium, which thus becomes more and more saturated with silicon; and at length a point is obtained at which the excess of silicon separates from the melted aluminium in large beautiful needles, having a dark iron-grey colour, reddish by reflected light, and exhibiting iridescence like that of iron-glance. These crystals appear to be derived from a rhombic octahedron, and often, like the diamond, exhibit curved faces. They are very hard, and capable of scratching or cutting glass (Deville). An easier method of obtaining crystallised silicon is to introduce into a red-hot earthen crucible a mixture of 3 pts. potassic silicofluoride, 1 pt. of sodium in small pieces, and 4 pts. of granulated zinc. The mixture must be kept at a red heat, but below the temperature required to volatilise the zinc, till the slag is completely melted; then left to cool slowly. The mass of zinc thus obtained contains long needles of silicon formed of octahedrons (? rhombic) inserted one into the other. Much of the zinc may be extracted by partial fusion at a low temperature, and the zinc which runs from the pasty mass, in which the silicon is retained, may be employed again in a similar operation. The zinc, which still adheres to the silicon, may be removed by digestion, first in hydrochloric, and afterwards in boiling nitric acid. If a very high temperature be employed in the operation, the whole of the zinc may be expelled, and the silicon obtained in the fused state. Deville and Caron have in this way fused several hundred grammes of silicon under a layer of potassic silicofluoride, at a temperature near the melting-point of cast-iron, and have cast it into large cylindrical bars, without sensible loss by oxidation. These bars exhibited a brilliant surface, which was not altered by exposure to the air (Ann. Ch. Phys. [3] lxiii. 26; lxvii. 441); see also Robbins (*Chem. News*, v. 102).

SILICON, BROMIDE OF. $SiBr^4$.—This compound, discovered by Serullas, is produced by passing bromine-vapour over an intimate mixture of silica and charcoal, heated to redness in a porcelain tube: it is purified by agitation with mercury, and distillation. Colourless liquid, of specific gravity 2·813, and having a pungent odour. It solidifies at 12° to 15° to an opaque, white, slightly nacreous mass; boils at 153·4° (under a pressure of 762 mm.), fumes very strongly in moist air, and in contact with water is immediately resolved into hydrobromic acid and gelatinous silica. Heated with potassium, it decomposes with detonation.

Silicohydric Bromide, $Si^3H^4Br^{10} = 3SiBr^2.4HCl$, is obtained by passing hydrobromic acid gas over ignited crystalline silicon, and passing the evolved vapours through a U-tube, cooled with ice and salt. When purified from free bromine by agitation with mercury, it is a colourless liquid, of specific gravity about 2·5; it fumes strongly in the air, and is instantly decomposed by water, yielding hydrobromic acid, and the corresponding hydrated oxide, $Si^3H^4O^5$, which forms a film on the surface, and for a while protects the remaining bromine-compound from further decomposition. (Wöhler and Buff, Ann. Ch. Pharm. civ. 99.)

SILICON, CHLORIDE OF. $SiCl^4$.—This compound is formed when silicon is heated in chlorine gas; but the best mode of preparing it is to mix finely-powdered silica to a paste with oil and charcoal, heat the mixture in a covered crucible, and ignite the charred mass in a porcelain tube, through which a current of chlorine is passed:

$$SiO^2 + 2Cl^2 + C^2 = 2CO + SiCl^4.$$

The product is received in vessels cooled by a freezing mixture.

Chloride of silicon, or silicic chloride, is a transparent colourless liquid, of specific gravity 1·5237 at 0°. It remains liquid at − 20°, boils at 50° (Serullas). Vapour-density: obs. = 5·939 (Dumas); calc. = 5·8905. The vapour has a suffocating odour, and reddens litmus.

Chloride of silicon is quickly decomposed by *water*, yielding hydrochloric acid and silica, a considerable quantity of which remains dissolved if the water is in large proportion. *Potassium*, heated in the vapour, decomposes it with separation of silicon. Fused potassium dropped upon the liquid chloride causes an explosion.

Silicohydric chloride, $Si^3H^4Cl^{10} = 3SiCl^2.4HCl$, analogous to silicohydric bromide, is prepared in like manner by passing hydrochloric acid gas over crystallised silicon heated to barely visible redness, and condensing the product in a U-tube cooled to 0°. It is a colourless very mobile liquid, of specific gravity 1·65, boiling at about 42°. It fumes strongly when exposed to the air, depositing a white film on surrounding bodies, and emitting a suffocating vapour. It is highly inflammable, and burns with a greenish feebly luminous flame, depositing silica and emitting hydrochloric acid. The vapour mixed with oxygen explodes violently on transmission of an electric spark, depositing silica, and yielding hydrochloric acid and tetrachloride of silicon. It may be boiled over sodium without decomposition—hence it does not appear to contain ready-formed hydrochloric acid; a similar observation applies to the bromide. When passed through a red-hot tube, it is resolved into a mixture of hydrochloric acid and the tetrachloride, whilst half the silicon is deposited in the form of a brown, amorphous, metallic-shining crust. Water decomposes it immediately, with great rise of temperature, forming hydrochloric acid and the corresponding hydrated oxide, called *leucone*: $Si^3H^4Cl^{10} + 5H^2O = Si^3H^4O^5 + 10HCl$. (Wöhler and Buff, Ann. Ch. Pharm. civ. 94.)

SILICON, DETECTION AND ESTIMATION OF. The methods of analysing compounds, in which silicon occurs as silicic acid, have been already detailed (p. 245).

The **chloride, bromide,** and **iodide** of silicon are completely decomposed by water; and on evaporating the liquid to dryness, the whole of the resulting hydrochloric, hydrobromic, or hydriodic acid goes off, and the silica remains, and may be weighed. The quantity of chlorine, &c. may also be directly determined by precipitation with nitrate of silver.

When **fluoride of silicon** is decomposed by water, part of the silica is precipitated, while another portion remains dissolved, as silicofluoric acid: $2HF.SiF^4$. The precipitated silica is separated by filtration after addition of alcohol, and the silicofluoric acid may be completely precipitated from the filtrate by addition of chloride of potassium. The precipitated silicofluoride of potassium is collected on a filter, washed with a mixture of equal volumes of alcohol and water, then dried at 100°, and weighed; and the quantity of silicon (or the corresponding quantity of silica) contained in it is determined by calculation. As the liquid filtered from the precipitated silicofluoride may still contain silica (which in the precipitated state is somewhat soluble in water, p. 241), it must be evaporated to dryness, the residue digested with water, and the silica that remains undissolved, collected and weighed.

Metallic silicofluorides are most easily analysed by heating them with strong sulphuric acid, whereby the whole of the silicon and fluorine are driven off in the form of silicic fluoride and hydrofluoric acid, while the metal remains as sulphate, which may be weighed, after the excess of sulphuric acid has been expelled by heat, aided, if necessary, by addition of carbonate of ammonium; the quantity of metal thence determined, gives the quantity of metallic fluoride in the compound $2MF.SiF^4$ or $M''F^2.SiF^4$.

If it be desired to determine directly the quantity of silicic fluoride, the silicofluoride may be decomposed by boiling it with a slight excess of sodic carbonate, whereby fluoride of sodium is formed, carbonic anhydride is evolved, and the metal of the silicofluoride is precipitated as oxide, mixed with the silica. These may be separated by the usual methods, and the fluorine precipitated by chloride of calcium (ii. 674). The same method must be resorted to if the silicofluoride to be analysed is in solution, or if it is mixed with other salts. (H. **Rose**, *Chimie Analytique*, ii. 888.)

The decomposition of silicofluorides by ignition does not yield very exact results; for although the whole of the fluoride of silicon is ultimately expelled, and the metallic fluoride remains, the weight of the latter can seldom be determined exactly, because the escaping fluoride of silicon being decomposed by the moisture of the air, or by water evolved from the lamp or other source of heat, a deposition of silica takes place on the crucible, and increases its weight. (H. **Rose**.)

Atomic weight of Silicon.—Berzelius regarded silica as a trioxide, SiO^3, and represented the chloride, bromide, &c. by the corresponding formulæ, $SiCl^3$, $SiBr^3$, &c. L. **Gmelin**, in his *Handbook* (iii. 352), adopted for silica the formula SiO^2, on account of the greater simplicity of the formulæ which it yields for the compounds of silicon both natural and artificial. This view, which amounts to regarding silicon as tetratomic, is corroborated by the vapour-densities of the chloride and fluoride of silicon, and by the composition of the silicic ethers (p. 263). The vapour-density of silicic chloride, as determined by Dumas, is 5·939, and that of the fluoride 3·60. Now if these compounds be represented by the tetratomic formulæ $SiCl^4$ and SiF^4 [Si = 28], their vapours will exhibit the normal condensation to 2 volumes, whereas the formulæ $SiCl^3$ and SiF^3 [Si = 21] would represent a condensation to 1½ volume: thus—

$$\text{Chloride, } SiCl^4;\quad \frac{28 + 4\,.\,35\cdot5}{2} \times 0\cdot0693 = 5\cdot8995.$$

$$\text{,,}\quad SiCl^3;\quad \frac{21 + 3\,.\,35\cdot5}{1\cdot5} \times 0\cdot0693 = 5\cdot8905.$$

$$\text{Fluoride, } SiF^4;\quad \frac{28 + 4\,.\,19}{2} \times 0\cdot0693 = 3\cdot604.$$

$$\text{,,}\quad SiF^3;\quad \frac{21 + 3\cdot195}{1\cdot5} \times 0\cdot0693 = 3\cdot604.$$

The older numerical determinations of the atomic weight of silicon by Berzelius, depending on the analyses of certain silicates and of cast-iron containing silicon, did not yield accordant results. By the analysis of silicofluoride of barium (100 pts. of the dry salt, decomposed by sulphuric acid, yielding 82·933 pts. sulphate of barium) Berzelius obtained Si (tetratomic) = 27·54. More exact results are obtained by decomposing chloride of silicon with nitrate of silver. **Pelouze** (Ann. Ch. Pharm. lvi. 202) found that 3·685 pts. of silver dissolved in nitric acid, precipitated the chlorine from 1·454 pts. chloride of silicon; whence Si = 28·48. **Dumas** (*ibid.* cxiii. 31), from the mean of three experiments conducted on the same principle, obtained the number 28·02.

SILICON, FLUORIDE OF. SiF^4.—A gaseous compound, produced whenever hydrofluoric acid comes in contact with silica or any silicious substance, such as glass, and therefore also when a mixture of a fluoride with silica or a silicate is heated with sulphuric acid. The reaction is,

$$4HF + SiO^2 = 2H^2O + SiF^4.$$

To prepare it, powdered fluor-spar, mixed with sand or finely-pounded glass, is gently heated in a flask with strong sulphuric acid, and the gas is collected over mercury in dry glass jars. If the receivers are coated with a film of moisture, they become coated with an opaque deposit of silica, which cannot be removed.

Fluoride of silicon is a colourless gas, having a specific gravity of 3·60, and a highly pungent and suffocating odour, like that of hydrochloric acid. According to J. Davy, it reddens litmus-paper even when perfectly dry. It liquefies under very strong pressure (Faraday), and solidifies at $-140°$ (Natterer). It is not inflammable, but extinguishes a lighted taper. It fumes strongly in the air, and is absorbed in large quantity by water, which at the same time decomposes it into silica and silicofluoric acid:

$$3SiF^4 + 2H^2O = 2H^2SiF^6 + SiO^2.$$

Aqueous *alkalis* and *alkaline earths* either act like water, precipitating only one-third of the silicon as silica, and forming a silicofluoride, $\left.\begin{matrix}M^2\\M''\end{matrix}\right\} SiF^6$, as with potash; or they precipitate the whole of the silica, and form a metallic fluoride, as is the case with soda. Many *metallic oxides* in the anhydrous state absorb gaseous fluoride of silicon, producing heat and sometimes even flame, and apparently forming a mixture of silica and metallic fluoride.—Burnt *lime*, immersed in the gas, becomes red-hot throughout its whole mass.—*Potassium*, at ordinary temperatures, acts but slightly on the gas; but if heated till it melts, it blackens, and burns with a dark-red flame, absorbing a portion of the gas, and yielding a dark-brown brittle mass (Gay-Lussac and Thénard). Sodium acts in a similar manner.

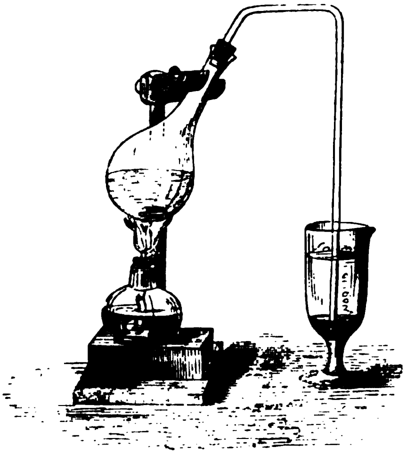
Fluoride of silicon combines with twice its own volume of *ammonia-gas*, forming a volatile crystalline compound, $2NH^3.SiF^4$, which is decomposed by water, yielding silica and a solution of fluoride and silicofluoride of ammonium (J. Davy):

$$2(2NH^3.SiF^4) + 2H^2O = 2NH^4F + (NH^4)^2SiF^6 + SiO^2.$$

Absolute alcohol absorbs fluoride of silicon, forming a liquid called silicofluoric or fluosilicic alcohol, consisting of a mixture of tetrethylic silicate and silicofluoric acid. To obtain a saturated solution, the alcohol must be kept cool. (Knop and Wolf, Chem. Centr. 1861, p. 822; Jahresb. 1861, p. 207.)

Silicofluoric acid, $Si^2H^2F^6 = 2HF.SiF^4$.—An acid produced by the action of water on gaseous fluoride of silicon. To prepare it, the generating flask is fitted with a wide glass tube, dipping under mercury at the bottom of a glass jar, as in *fig.* 743. Water is then poured into the glass, and heat applied to the mixture in the flask. The object of making the end of the tube dip under mercury, is to prevent it from being stopped up by the deposited silica. Each bubble of gas, as it rises through the water, is decomposed, as above explained, into silicofluoric acid and free silica—the former dissolving, while the latter is set free in the solid state, and forms a silicious envelope round the bubble as it rises above the surface of the mercury; ultimately, the liquid sets into a gelatinous mass. When sufficiently saturated, it is separated from the silica by pressure between linen, and finally by filtration through paper.

Fig. 743.



An easier method of obtaining the acid in large quantities is to dissolve silica in dilute hydrofluoric acid.

A saturated solution of silicofluoric acid forms a very sour fuming liquid, which gradually evaporates at 40° in platinum vessels without leaving any residue. It does not attack glass except when evaporated upon it; in that case the fluoride of silicon goes off first, leaving hydrofluoric acid, which corrodes the glass, and ultimately evaporates also as fluoride of silicon.

According to Stolba (J. pr. Chem. xc. 193), the specific gravity of the aqueous acid increases regularly with its strength, as shown by the following numbers:—

Percentage of H^2SiF^6 . .	0·5	1	1·5	2	5	10
Specific gravity at 17·5° . .	1·0040	1·0080	1·0120	1·0161	1·0407	1·0834

Silicofluorides. $2MF.SiF^4$, or $M''F^2.SiF^4$.—These salts are produced:—1. By dissolving a metallic oxide, hydrate or carbonate (or, in the case of iron or zinc, the simple metal) in silicofluoric acid till the liquid is nearly saturated,—when, if the compound is not insoluble, it is separated on evaporating the liquid in a platinum-vessel. If it gelatinises from excess of silica, a small quantity of hydrofluoric acid must be added, and this, on further evaporation, volatilises with the silica in the form of silicic fluoride.—2. By the action of silicic fluoride on metallic fluorides (either dry or in solution), which readily absorb the gas: or on metallic oxides or carbonates slightly moistened with water. In the latter case a portion of the silicon is separated in the form of silica.

Most silicofluorides are easily soluble in water; only those of sodium, lithium, barium, calcium, and yttrium, are sparingly soluble. The solutions frequently yield hydrated crystals. Many of these crystals lose their water by efflorescence on exposure to the air, and all of them undergo this change when heated.

The silicofluorides redden litmus, and for the most part have an acid and bitter taste. By prolonged ignition, they give up the whole of the fluoride of silicon, the metallic fluoride remaining behind in the pure state. If they contain water, the gaseous fluoride of silicon, as it escapes, is accompanied by a white sublimate in the form of minute drops, which on exposure to moist air deposit silica.

The silicofluorides, many of them at least, are resolved by ignition with *potassium* into silicon and fluoride of potassium, whilst the metallic fluoride previously in combination with the fluoride of silicon, either remains unaltered, or gives up its fluorine also to the potassium. The action of *iron* at a red heat is similar to that of potassium (Berzelius). With *oil of vitriol*, the silicofluorides at first evolve gaseous fluoride of silicon with effervescence; then, at a temperature which, in the case of the calcium and barium-compound, exceeds 100°, anhydrous hydrofluoric acid is evolved. *Hydrochloric* and *nitric acids* expel only a part of the hydrofluosilicic acid. The silicofluorides are decomposed by excess of alkali, silica being precipitated, and a metallic fluoride remaining in solution: *e.g.*—

$$2KF.SiF^4 + 4KHO = SiO^2 + 6KF + 2H^2O.$$

Silicofluorides of the Alkali-metals.—The *ammonium-salt*, $(NH^4)^2SiF^6 = 2NH^4F.SiF^4$, is produced by neutralising silicofluoric acid with ammonia, avoiding an excess. The filtered liquid yields the salt by spontaneous evaporation, in large, transparent, shining, four- or six-sided prisms, containing water of crystallisation.

The *lithium-salt*, $2LiF.SiF^4$, crystallises from solution in silicofluoric acid in small transparent grains, which under the microscope present the appearance of six-sided prisms. It has a slightly acid and bitter taste, melts at a red heat, and obstinately retains its fluoride of silicon. Pure water dissolves it very slowly; acidulated water more readily.

The *potassium-salt*, $2KF.SiF^4$, is obtained as a transparent gelatinous precipitate, when silicofluoric acid is added to any salt of potassium; when dry it forms an earthy-looking powder. It is one of the least soluble of the potassium-salts, and consequently silicofluoric acid is often used to precipitate potassium from the solutions of its salts; in this manner chloric acid is sometimes prepared from chlorate of potassium. According to Stolba (J. pr. Chem. xc. 193), it has a specific gravity of 2·6649—2·6655 at 17·5°, and dissolves in 833·1 pts. of water at that temperature, and in 104·8 pts. at the boiling heat. It is insoluble in alcohol. The salt melts at a low red heat, and boils at a higher temperature, slowly evolving gaseous fluoride of silicon. Heated with potassium, it yields silicon and fluoride of potassium.

The *sodium-salt*, $2NaF.SiF^4$, resembles the potassium-salt, and is obtained in like manner. According to Stolba, it has a density of 2·7547 at 17·5°, dissolves in 153·3 pts. water at that temperature, and in 40·66 pts. at its boiling heat (101°). It has a great tendency to form supersaturated solutions, and may be used as a test for potassium-salts when the solutions of the latter are not too dilute. The solutions of the potassic and sodic silicofluorides, when slowly evaporated, deposit the salts in ring-shaped crusts on the side of the vessel (Stolba). The sodium-salt is insoluble in alcohol, whether strong or dilute.

Silicofluorides of the Earth-metals.—The *barium-salt*, $Ba''F^2.SiF^4$, is produced on adding silicofluoric acid to a soluble barium-salt, and is quickly deposited in microscopic crystals, insoluble in excess of the acid. It is decomposed by ignition, fluoride of silicon going off and fluoride of barium remaining.—According to Fresenius (Ann. Ch. Pharm. lix. 117), it dissolves in 3,802 pts. of pure water, and in 733 pts. of water acidulated with hydrochloric acid.—The *strontium-salt* separates from a solution of strontium-carbonate in silicofluoric acid, on evaporation or cooling, in short hydrated rhombic prisms, with dihedral summits resting on the acute lateral edges. It is much more soluble than the barium-salt, so that silicofluoric acid may be used to distinguish barium from strontium in solution.—The *calcium-salt* crystallises in four-sided obliquely truncated prisms, which are decomposed by water, yielding on the one hand an insoluble residue of silicon and fluoride of calcium, and on the other silicofluoric acid, by which the remainder of the silicofluoride is dissolved without decomposition (Berzelius).—The *glucinum-salt* is easily soluble in water, and if the solution contains excess of acid, it remains, after the volatilisation of the latter, in hard white masses resembling porcelain (Berzelius).—The *magnesium-salt*, $Mg''F^2.SiF^4$, is a transparent, yellowish, gummy mass, easily soluble in water (Berzelius).—The *yttrium-salt* is insoluble in pure water, but soluble in water containing hydrochloric acid, and separates on evaporation (Berzelius); decomposed by evaporation (Popp).—The *zirconium-salt* forms white pearly crystals, very soluble in water; the solution becomes turbid on boiling, but the greater part of the salt remains dissolved.

Silicofluorides of Heavy Metals.—*Antimony-salt.* A solution of antimonious oxide in silicofluoric acid crystallises by slow evaporation in prisms, which crumble to powder when dried in the air, and dissolve readily in excess of the acid (Berzelius). The *cadmium-salt* forms long, transparent, efflorescent prisms, very soluble in water. (Berzelius.)

Chromic salt.—A solution of chromic oxide in silicofluoric acid, yields by evaporation a transparent, green, amorphous, deliquescent mass, which, if it contains excess of acid, swells up in the fire like alum, and again deliquesces on exposure to the air. (Berzelius.)

Cobalt-salt, $Co''F^2.SiF^4.7H^2O$.—Pale-red rhombohedrons, easily soluble in water. (Berzelius.)

Copper-salts.—The cuprous salt, $2CuF.SiF^4$, is copper-coloured, resembling cuprous fluoride, and behaves like the latter when exposed in the moist state to the air. When somewhat strongly heated, it melts, and gives off fluoride of silica with ebullitions. (Berzelius.)

Cupric Silicofluoride is obtained by spontaneous evaporation of a solution of cupric oxide in silicofluoric acid, in transparent octahedrons and hexagonal prisms, containing $Cu''F^2.SiF^4.7H^2O$, which effloresce in the air, becoming light-blue and opaque, and giving off 2 at. water, and are easily soluble in water. (Berzelius). Knop and Wolf prepare this salt by adding precipitated cupric oxide in slight excess to fluosilicic alcohol (p. 270), diluted with 3 or 4 times its volume of absolute alcohol. A pale-blue crystalline powder is thereby produced, the filtered aqueous solution of which contains pure cupric silicofluoride, and yields, with potassium and barium-salts, precipitates having the usual composition of the silicofluorides, $M^2F.SiF^4$. But by adding precipitated cupric oxide to fluosilicic alcohol diluted with eight times its volume of water, and heated to 50°—60°, a solution is obtained, which yields by double decomposition, compounds containing silicon and fluorine, but of more complex constitution than the ordinary silicofluorides.—Another series of fluosilicic compounds is obtained by decomposing the solution of cupric silicofluoride, or of the copper-salt last described, with zinc or iron. The zinc or iron-salt thus obtained yields, by double decomposition, the third series of salts just mentioned. (Knop and Wolf, Jahresb. 1861, p. 207.)

Silicofluorides of Iron.—The ferrous salt, $Fe''F^2.SiF^4$, is obtained by spontaneous evaporation of a solution of iron in silicofluoric acid, in pale bluish-green six-sided prisms, very soluble in water.—The ferric salt, $2Fe'''F^3.3SiF^4$, remains on evaporating a solution of ferric hydrate in silicofluoric acid, as a yellowish jelly, which dries up to a transparent gummy mass, completely soluble in water. (Berzelius.)

The *lead-salt*, $Pb''F^2.SiF^4$, dries up to a translucent gum, which tastes like other lead-salts, and redissolves completely in water. (Berzelius.)

The *manganous salt*, $Mn''F^2.SiF^4.7H^2O$, crystallises from a very strong solution in long regular six-sided prisms, or by slower evaporation in shorter prisms and rhombohedrons. It has a very light-red colour, and is easily soluble in water. When distilled, it first gives off its 7 at. water, and then gaseous fluoride of silicon. (Berzelius.)

Silicofluorides of Mercury.—The mercurous salt, $2HgF.SiF^4$, formed by digesting recently precipitated mercurous oxide with silicofluoric acid, separates on evaporation in small crystals, sparingly soluble in water.—The mercuric salt, $Hg''F^2.SiF^4$, obtained by dissolving mercuric oxide in the acid, forms small pale-yellow needles, which when distilled give off first gaseous fluoride of silicon, then mercuric fluoride. They dissolve completely in acidulated water, but are decomposed by pure water, yielding an acid solution and an insoluble basic salt. (Berzelius.)

Silicofluorides of Molybdenum.—A solution of molybdous hydrate in excess of silicofluoric acid dries up when heated to a black neutral compound, which redissolves in the aqueous acid.—A solution of molybdic hydrate in silicofluoric acid acquires a bluish tinge when left to evaporate, and yields a black uncrystallisable mass, from which water dissolves out the blue salt, leaving the neutral compound in the form of a jet-black powder.

The yellowish solution of molybdic trioxide in silicofluoric acid leaves, when evaporated, a lemon-yellow opaque substance, which redissolves for the most part in water. (Berzelius.)

Platinic Silicofluoride.—The yellow solution of platinic hydrate in silicofluoric acid dries up to a yellowish-brown gum, which partly redissolves in water, leaving a brown basic salt. (Berzelius.)

Silver-salt, $2AgF.SiF^4$.—A solution of silver-oxide in silicofluoric acid yields deliquescent granular crystals. Ammonia added to the solution throws down a light-yellow basic salt, which, when treated with excess of ammonia, is converted into silicate of silver. (Berzelius.)

Stannic Silicofluoride, $SnF^4.2SiF^4$, crystallises in long prisms, very soluble in water. (Berzelius.)

Uranous Silicofluoride is obtained as a pale-green gelatinous precipitate on adding silicofluoric acid to uranous chloride. When heated in a tube, it yields water, hydrofluoric acid, and sublimed silica. (Rammelsberg.)

Vanadic Silicofluorides.—The blue solution of vanadic dioxide in silicofluoric acid leaves, when quickly evaporated, a blue substance, which, at a moderate heat, swells up to a pale-blue porous mass. The solution, if left to evaporate spontaneously, turns green, and leaves a syrupy liquid containing crystals.—Vanadic trioxide forms with silicofluoric acid a red solution, which leaves on evaporation an orange-yellow mass, only partially soluble in water. (Berzelius.)

Silicofluoride of Zinc.—A solution of zinc-oxide in silicofluoric acid yields, by evaporation at a high temperature, three- and six-sided transparent colourless prisms, containing $Zn''F^2.SiF^4$, permanent in the air, and very soluble in water. (Berzelius.)

SILICON, HYDRIDE OF. SiH (?). *Silicic Hydride, Hydric Silicide, Siliciuretted Hydrogen.* (Wöhler and Buff, Ann. Ch. Pharm. cii. 128; ciii. 218; civ. 94; cvii. 112; Jahresb. 1857, p. 166; 1858, p. 142.)—Silicon forms with hydrogen a gaseous compound, which is not known in the pure state, but is obtained, mixed with a large quantity of free hydrogen, when a wire or plate of aluminium containing silicon is connected with the positive pole of a voltaic battery (a Bunsen's battery of 8 to 12 cells), and made to decompose a solution of chloride of sodium. The aluminium then dissolves as chloride, a considerable quantity of gas is evolved at its surface, and many of the gas-bubbles, as they escape into the air, take fire spontaneously, burning with a white light, and diffusing a white fume. The formation of the siliciuretted hydrogen appears to be due to a secondary action accompanying the electrolysis of the saline solution. The aluminium forming the positive pole of the battery combines with the chlorine and dissolves; but the quantity of aluminium removed is about one-fourth greater than that which is equivalent to the quantity of chlorine eliminated from the solution. This excess of aluminium is found to be removed in the form of alumina, formed by the combination of the metal with oxygen derived from the water. The equivalent quantity of hydrogen is of course set free, and part of it enters into combination with the silicon contained in the aluminium.

Siliciuretted hydrogen is likewise produced in the decomposition of certain metallic silicides by hydrochloric acid, and by the action of heat on the hydrates of silicon. The best alloy for preparing it is a silicide of magnesium, obtained by intimately mixing 40 pts. of fused chloride of magnesium, 35 pts. dried silicofluoride of sodium, and 10 pts. fused chloride of sodium, stirring the mixture in a warm dry tube with 20 pts. of sodium in small fragments, throwing the whole into a red-hot hessian crucible, which is to be immediately covered, and heating it till the vapours of sodium cease to burn. The greyish-black scoriaceous mass thus produced contains, according to Wöhler, two silicides of magnesium, one of which, when treated with hydrochloric acid or solution of sal-ammoniac, gives off siliciuretted hydrogen, while the other yields with hydrochloric acid nothing but free hydrogen and hydrated oxide of silicon.

To obtain the gas, the coarsely pulverised mass is introduced into a two-necked bottle, one tubulure of which is fitted with a straight funnel-tube reaching to the bottom, while the other is provided with a gas-delivery-tube. The bottle is filled up with de-aërated water, and the delivery-tube is made to dip under water in the pneumatic trough, care being taken that not a bubble of air shall remain either in the bottle or in the tube. Strong hydrochloric acid is then poured in through the funnel-tube, and the gas, which is rapidly evolved, is collected in a glass jar filled with de-aërated water. The froth which passes over with it quickly subsides, so that the pure gas may be transferred into another receiver, and dried, if necessary, over chloride of calcium.

Siliciuretted hydrogen mixed with free hydrogen is a colourless gas, insoluble in pure de-aërated water and in salt water; but over water containing air it is decomposed, forming white clouds of silica, and losing its spontaneous inflammability. If it be passed into the air in single bubbles, each bubble takes fire spontaneously, and with explosion, burning with a white flame and separation of silica, which rises in beautiful rings, often coloured brownish by admixture of amorphous silicon. When set on fire, as it issues from a tube, it burns with a brilliant white flame. On opening a glass jar filled with it in the air, it takes fire, the flame gradually passing down the jar, the inner surface of which becomes coated with brown silicon.

The gas, when heated by itself, is decomposed into amorphous silicon and free hydrogen, and at the same time increases in volume, showing that the hydrogen in the compound is in a condensed state. It has not been analysed quantitatively. A piece of porcelain introduced into the flame becomes coated with brown silicon; and, on passing the gas through a glass tube heated to low redness, the interior becomes coated with a dark-brown opaque mirror. The gas is easily decomposed by chlorine. It is not altered by dilute hydrochloric or sulphuric acids. When shaken up with potash-ley, it is decomposed with increase of volume; soda and ammonia do not appear to act upon it. From a solution of cupric sulphate, siliciuretted hydrogen immediately precipitates silicide of copper (p. 265); from nitrate of silver it throws down grey metallic silver mixed with a black substance, probably silicide of silver; from chloride of palladium it throws down black-grey metallic palladium, free from silicon. It does not precipitate acetate of lead or chloride of platinum.

SILICON, IODIDES OF. The iodide of silicon, corresponding to the tetrachloride, has not been obtained: silicon does not unite directly with iodine.

Iodide of Silicon and Hydrogen, $Si^3H^4I^{10}$, is obtained, like the corresponding chlorine and bromine compounds (pp. 267, 268), by passing hydriodic acid gas over heated crystalline silicon, and collects at the colder end of the condensing-tube as a dark-red brittle mass, which fuses readily, and solidifies in the crystalline form on cooling. At a stronger heat it boils, and distils without decomposition. It fumes strongly in the air, assuming at first a bright vermillion colour, but ultimately becoming snow-white. In water it immediately becomes vermillion-coloured, but is only slowly decomposed. Sulphide of carbon dissolves it in large quantity, forming a blood-red solution, which, when concentrated in a retort, deposits the compound on cooling in dark-red crystals. Caustic soda-solution dissolves it, with evolution of hydrogen. (Wöhler and Buff, Ann. Ch. Pharm. civ. 99.)

SILICON, NITRIDE OF. (Deville and Wöhler, Ann. Ch. Pharm. civ. 256; cx. 248.)—Obtained by the action of ammonia on silicic chloride, and by exposing crystalline silicon to an intense heat in nitrogen gas or atmospheric air. Its composition has not been ascertained. It is a white amorphous mass, infusible and unalterable at the highest temperatures, and not oxidised even by ignition in contact with the air. It is not acted on by any acid except hydrofluoric acid, which dissolves it with formation of silicofluoride of ammonium. When strongly ignited in a stream of aqueous vapour and carbonic anhydride, it is decomposed, yielding carbonate of ammonium; it likewise decomposes slowly in moist air, as indicated by the odour of ammonia which it evolves. Aqueous alkalis do not act upon it, but when fused with hydrate of potassium, it forms silicate of potassium, with evolution of ammonia. When fused with carbonate of potassium, it yields silicate and cyanate of potassium; also cyanide, if the nitride of silicon is in excess. When heated with red oxide of lead, it reduces the lead with incandescence, and forms nitrous anhydride.

SILICON, OXIDES AND HYDRATES OF. The only known anhydrous oxide of silicon is the dioxide or silica, SiO^2, already described (p. 240). There is, however, a compound of silicon, hydrogen, and oxygen, $Si^3H^4O^5$, which may be supposed to contain the protoxide of silicon, SiO, and two others (p. 275), which may be formulated as hydrates of a tetrasilicic oxide—viz., $Si^4H^4O^8 = Si^4O.2H^2O$, and $Si^4H^8O^6 = Si^4O.4H^2O$.

a. Leucone, $Si^3H^4O^5 = 3SiO.2H^2O$. (Wöhler and Buff, Ann. Ch. Pharm. civ.

101.—Wöhler, *ibid.* cxxvii. 257.)—Produced by the action of water on the corresponding chlorine or bromine compound (pp. 267, 268), also by the action of water on chryseone (*infra*) under the influence of light. The best mode of preparing it is to heat crystalline silicon to redness in a stream of chlorine, and pass the resulting vapour of silicohydric chloride into water. It must be washed with ice-cold water, strongly pressed between filtering-paper, and dried over oil of vitriol. As thus obtained, it is a snow-white, bulky, amorphous substance, which floats on water, but sinks in ether; by the action of water on chryseone, it is obtained in laminæ having the form of the latter. It is permanent at ordinary temperatures, and may be heated to 300° without alteration; but when more strongly heated out of contact with air, it gives off hydrogen, sometimes mixed with siliciuretted hydrogen. When heated in the air, or in oxygen gas, it glows with a bright light, and leaves silica coloured brown by amorphous silicon, if the supply of oxygen is limited. It is slightly soluble in water, but the solution gradually decomposes, giving off hydrogen gas. Caustic alkalis, even ammonia, and alkaline carbonates, dissolve it, with rapid evolution of hydrogen and formation of alkaline silicates. When recently prepared, it acts as a powerful reducing agent, separating gold and palladium from the solutions of their chlorides, selenium and tellurium from selenious and tellurous acid, &c. In solution of silver-nitrate it immediately turns light-brown, and, on subsequent addition of ammonia, is converted into black silicate of silver.

β. *Chryseone*, $Si^4H^4O^3$ (?). *Silicone.** (Wöhler, Ann. Ch. Pharm. cxxvii. 257; Jahresb. 1863, p. 205.)—Produced by the action of strong hydrochloric acid on silicide of calcium (p. 265). The finely divided silicide is digested with fuming hydrochloric acid in a cooled vessel and in a dark place for several hours, till hydrogen is no longer evolved; the liquid is diluted with 6 or 8 volumes of water, and filtered; and the washed residue is dried over sulphuric acid in a vacuum, and in the dark. If the hydrochloric acid is not quite concentrated, the product is mixed with the following compound, γ.

Chryseone forms bright orange-coloured laminæ, which are pseudomorphs after the crystalline silicide of calcium. It is insoluble in water, alcohol, tetrachloride of silicon, trichloride of phosphorus, and sulphide of carbon. When heated it becomes transiently darker, and at a higher temperature burns with a slight detonation and with scintillation, leaving silica coloured brown by amorphous silicon. When heated in a close vessel, it gives off hydrogen, likewise leaving silica and silicon. If mixed with the compound γ, it detonates even when heated in a tube, and gives off spontaneously inflammable siliciuretted hydrogen. Heated to 100°, by itself or with water, it slowly gives off hydrogen and becomes paler; heated to 190° with water, in a sealed tube, it is quickly and completely converted into laminar silica, while the tube contains compressed hydrogen gas. In the dark it remains unaltered even when moist, in diffused daylight it becomes continually paler, and in direct sunshine, even under water, it is quickly converted into leucone, with evolution of hydrogen. It is not attacked by chlorine, fuming nitric acid, or strong sulphuric acid, even when heated. With hydrofluoric acid it becomes hot, turns white, and finally dissolves. By alkalis, even by very dilute ammonia, and more slowly by alkaline carbonates, it is converted, with rise of temperature and violent evolution of hydrogen, into silica. In presence of alkali it reduces the salts of several metals. In the solution of a copper or silver-salt it quickly turns black; in chloride of gold, brown; from chloride of palladium, osmic acid, and chloride of gold, on addition of alkali, it throws down black or violet-black powders, probably silicates containing lower oxides of those metals. From a solution of lead-oxide in soda-ley, it instantly precipitates the lead as a grey mass.

The results of the analysis of chryseone correspond partly with the formula $Si^4H^4O^3$, partly with $Si^6H^6O^4$. According to the first formula, its formation from silicide of calcium may be represented by the equation:

$$2CaSi^2 + 4HCl + 3H^2O = Si^4H^4O^3 + 3H^2 + 2CaCl^2.$$

γ. $Si^4H^8O^5$.—This compound, containing $2H^2O$ more than the preceding, is produced by the action of cold dilute hydrochloric acid on silicide of calcium. It forms colourless, transparent, nacreous laminæ, which, after washing and drying in a vacuum, take fire spontaneously in contact with the air, and burn with flame, leaving brown silica.

SILICON, SELENIDE OF. The selenide of silicon, analogous to silica, is not known. A silicohydric selenide, analogous to the oxygen-compound last described, is produced by treating silicide of calcium with a mixture of selenious and hydrochloric acids. It is a cinnabar-coloured substance, which smells of hydric selenide when dry, gives off hydrogen in contact with ammonia, and when heated by itself evolves hydric selenide and selenium, without explosion. (Wöhler.)

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* *Silicone* is the name originally given to this compound by Wöhler, but it is objectionable in English on account of its similarity to silicon. The name *chryseone*, indicating the colour of the compound, was proposed by Dr. Miller.

SILICON, SULPHIDES OF. The disulphide, SiS^2, is produced by the action of carbonic disulphide on silica at high temperatures, or more easily by passing the vapour of carbonic disulphide over a heated mixture of silica and carbon, prepared by moulding a mixture of silica and lampblack with oil into balls and igniting them. The sulphide of silicon is deposited in the colder parts of the tube, in long, white, silky, flexible, asbestiform needles, which may be volatilised in a stream of gas. In contact with moist air, or when heated in aqueous vapour, it decomposes quickly into sulphydric acid and amorphous anhydrous silica, which remains in the form of the sulphide. In water it dissolves completely, with evolution of sulphydric acid, and the solution, left to evaporate in the air, deposits the silica as a transparent vitreous hydrate resembling opal. Alcohol and ether act upon sulphide of silicon even in the cold, forming sulphuretted organic compounds. It is not decomposed by heating in hydrogen gas. Nitric acid decomposes it, with separation of sulphur, and formation of sulphuric acid and silica. (Frémy, Ann. Ch. Phys. [3] xxxviii. 314.)

Silicohydric sulphide, $Si^4H^8O^3$, analogous to the oxygen-compound γ, is produced by the action of excess of aqueous sulphurous acid, mixed with a little hydrochloric acid, on silicide of calcium, and separates in reddish-brown laminæ, while the liquid, which is brownish at first, suddenly becomes milky from separated sulphur. When dried in a vacuum and freed from sulphur by sulphide of carbon, it forms a light-brown powder with a greenish tinge. It smells persistently of sulphydric acid, burns like gunpowder when heated in the air, and explodes violently when heated in a tube, with incandescence and evolution of sulphydric acid. When cautiously heated it gives off sulphydric acid, and the residue, which is no longer explosive, evolves more sulphydric acid in contact with water. With ammonia it rapidly gives off hydrogen, and is converted into a white mixture of silica and sulphur. (Wöhler.)

SILICON, SULPHOCHLORIDE OF. $Si^2S^4Cl^8$? (Pierre, Ann. Ch. Pharm. lxix. 73.)—Obtained by passing a mixture of silicic chloride vapour and perfectly dry sulphydric acid gas through a red-hot porcelain tube, collecting the product in a cooled U-tube, leaving the liquid to clarify, then distilling it, and collecting apart that which passes over between 90° and 100°. It is a colourless, transparent, mobile liquid, having a pungent odour, boiling at 100°, and distilling without residue. Specific gravity = 1·45. It is decomposed by water, yielding sulphydric and hydrochloric acids, silica, and free sulphur.

SILICON, TELLURIDES OF. A silicohydric telluride, analogous to the sulphur-compound above described, is produced by treating silicide of calcium with a dilute solution of tellurous acid in hydrochloric acid. It is a greyish-black powder, inodorous after drying. When heated it gives off hydrogen and tellurium, without explosion, and leaves a shining black residue, probably telluride of silicon, which when treated with ammonia or soda-ley, gives off hydrogen and forms a purple-red solution of alkaline telluride. (Wöhler.)

SILIQUA DULCIS, the so-called *St. John's-bread*, consists of the pods of *Ceratonia Siliqua* (L.), a tree indigenous in the South of Europe and the Levant. The kernels are enveloped in a sweet marrow-like substance, which has been analysed by Reinsch (Jahrb. pr. Pharm. v. 201) and Mercer (Pharm. J. Trans. 1857, p. 469), with the following results:—

	Reinsch.	Mercer.
Glucose	41·2	47·5
Albumin	20·8	3·2
Mucus	. .	4·7
Gum	10·4	
Pectin	7·2	
Tannin	2·0	
Fibrin	6·2 and starch	21·5
Water	12·0	21·0
Chlorophyll, Oil, Starch, and Ash	2·0	2·0

By fermenting the pods, Mercer obtained a quantity of brandy, amounting to one-fourth of their weight. Redtenbacher found butyric acid in the pods. Reinsch found, in 160 pts. of the kernels, 8 pts. starch, 2 sugar, 1·5 fatty oil, together with albumin, fibrin, wax, colouring matter, woody fibre, and other substances.

SILK. The fibrous substance in which the silkworm (the larva of *Phalæna Bombyx*

Mori) envelopes itself previous to passing into the chrysalis state. These insects possess a glandular apparatus called the *Sericterium*, serving for the secretion of a peculiar juice, which is discharged in fine threads, through two small apertures near the lower lip, and quickly solidifies in contact with the air. The solidified fibre consists of a thread of sericin or fibrin (i. 645; v. 235), coated with a yellowish waxy substance, the removal of which constitutes an important part of the process of silk-dyeing (i. 603; ii. 352.)

Silk may be distinguished from cotton and linen:—1. By its reaction with a concentrated *ammoniacal solution of nickel-oxide*, which dissolves it completely, forming a brownish-yellow solution, not precipitated by alkaline salts, sugar, or gum; acids, however, precipitate the silk completely in colourless flocks. Cotton, linen, and other forms of cellulose, on the contrary, are not altered even by several days' immersion in the nickel solution. Silk likewise dissolves in a concentrated ammoniacal solution of *cupric oxide*, and is but incompletely or not at all precipitated therefrom by alkali-salts, sugar, gum, or acids: cellulose, on the other hand, is completely precipitated from the same solution by these reagents (Schlossberger, Ann. Ch. Pharm. cvii. 21).—2. By immersing the fabric, for a few minutes, in a somewhat dilute solution of *picric acid* and then washing it carefully with water. Silk and other animal fibres are thereby turned yellow, whereas vegetable fibres remain white (Pohl, Wien, Akad. Ber. ix. 386). Strong *nitric acid* also turns animal fibres yellow, and does not produce that effect on vegetable fibres.—3. A solution of *stannic chloride* heated to 130°—150° turns linen and cotton black, but does not alter the colour of silk or wool. This test is of course applicable only to light-coloured fabrics (Maumené, Compt. rend. xxx. 447).—On the silk manufacture, see *Ure's Dictionary of Arts*, &c., iii. 654.

SILLIMANITE. A silicate of aluminium, $Al^2O^3.SiO^2$, identical in composition with cyanite and andalusite, occurring in veins in the gneiss of Saybrook, in Chester County, Connecticut, also at Fairfield, in New York. It forms triclinic crystals, usually indistinct, but cleaving perfectly parallel to the macrodiagonal; occurs also compact or loose, fibrous and columnar massive. It is brown, yellowish-grey, or colourless, with waxy lustre, vitreous on the cleavage-faces. Transparent to translucent on the edges only. Brittle. Hardness = 6—7. Specific gravity = 3·2—3·3. Infusible before the blowpipe. Insoluble in acids (Dana, ii. 265). For analyses see SILICATES (p. 255).

Bucholzite, from Chester County, Pennsylvania, and other localities in the United States, and *Fibrolite*, from the Carnatic, are fibrous varieties of sillimanite, of greyish, whitish, and pale-brown colour, with lustre approaching to adamantine.

SILVER. *Argent; Silber.* *Symbol*, Ag; *Atomic weight*, 108.

This metal is remarkable for its whiteness; hence its Greek name *ἄργυρος* from *ἄργος, white.* It is harder than gold and softer than copper. Its lustre, when polished, is nearly as great as that of steel. Its malleability is inferior only to that of gold among the heavy metals; it may be hammered into extremely thin sheet or *silver-leaf*, which is not more than $\frac{1}{100,000}$ of an inch thick. It is also highly ductile, and may be drawn into very fine wire, 400 feet of which weigh only one grain. By hammering and drawing, however, it readily becomes brittle, and requires to be more frequently annealed in working than gold does.

Silver has great tenacity, a wire two millimetres (0·0787 inch) in diameter being capable of supporting a load of nearly 85 kilogrammes (187 lbs.), that being the breaking weight. (See Baudrimont, Ann. Ch. Phys. [3] xxx. 304.)

The specific gravity of silver is 10·5, after being melted. (G. Rose.) Its density is increased to 10·57 by the coining process. The specific gravity of the finely divided metal, obtained by precipitation, is 10·62.

Silver crystallises in forms belonging to the regular system, generally in cubes, sometimes with faces of the octahedron.

The conductivity of silver for electricity and heat is greater than that of any other metal. (See ELECTRICITY, ii. 466; METALS iii. 936; and *ante*, p. 71). It decreases with the temperature. (See Wiedemann and Franz, Pogg. Ann. lxxxix. 497; Buff, Jahresb. 1847, p. 286; Becquerel, Ann. Ch. Phys. [3] xvii. 242; Langsdorff, Ann. Ch. Pharm. lxxxv. 155; Matthiesen, Pogg. Ann. ciii. 428; Benedict, Wien. Akad. Ber. xxv. 590; Jacobi, Petersb. Acad. Bull. xvii. 321; Arndtsen, Pogg. Ann. civ. 1; Clausius, *ibid*. p. 650). The specific heat of silver is 0·05701 (Regnault); 0·05507 (Dulong and Petit). The latent heat of fusion is 21·07 (Person, Ann. Ch. Phys. [3] xxiv. 265). Silver melts at a white heat; the temperature of fusion has been estimated at 1000° (Pouillet), 999° (Prinsep), and 1034° (Guyton Morveau). The melted metal gives off vapour to some extent at very high temperatures (Lampadius, J. pr. Chem. xvi. 204; Despretz, Comptes rend. lxviii. 362). The metal is volatilised more readily in the presence of arsenical and other vapours than when heated alone.

Silver does not combine with oxygen at the ordinary temperature, or, under ordinary circumstances, when heated in contact with atmospheric air. When the metal is melted upon ignited charcoal under a jet of oxygen, it burns with a conical flame, yellow below, purple at the middle, and blue above, while vapours of silver oxide are produced (Vauquelin). Silver is also oxidised under the influence of the electric spark; and when pulverulent, it is converted into peroxide by ozonised oxygen (Schönbein). When silver is melted in contact with alkaline or earthy silicates, it is oxidised to some extent and dissolved by the melted silicate. This is also the case when the finely divided metal is ignited with cupric oxide, or with arsenic or antimony: in the former case, cuprous oxide is formed; in the latter case, the silver-oxide combines with some arsenic or antimonic acid, and the more minutely the silver is divided the more readily does this oxidation take place. It is probable that silver is also oxidised to some extent in cupellation, and that the loss of silver experienced in that operation is mainly due to oxidation, the silver-oxide being in part volatilised, together with the lead fumes, and in part dissolved by the melted lead-oxide, and absorbed by the cupel.

Silver undergoes no change when heated in contact with melted alkaline nitrates or caustic alkalis, and for this reason silver crucibles are very useful in chemical operations with those substances which react with platinum under similar conditions.

When silver is kept melted for some time, at a high temperature, in contact with atmospheric air, it absorbs oxygen gas, and holds it in solution until just before the metal begins to solidify on cooling. The gas is then suddenly disengaged with effervescence, and particles of the metal are liable to be spirted or projected out of the crucible. The presence of a small amount of copper in the melted metal prevents the absorption of oxygen. Silver is capable of dissolving in this way 22 times its volume of oxygen.

Silver combines readily with *sulphur*, *selenium*, *phosphorus*, and *arsenic*. It decomposes *sulphuretted hydrogen* even at the ordinary temperature, and the surface of the metal becomes covered with a brown or black film of silver-sulphide. The discoloration of silver utensils and ornaments by exposure to the atmosphere generally consists in the formation of such a film of sulphide or, in some instances, of phosphide. Such stains may be removed by moistening the surface with a solution of alkaline cyanide and then washing well with water. When the discoloration is very considerable, it may be removed by immersing the metal in a boiling saturated solution of borax or strong caustic alkali, and placing a plate of zinc in contact with it for some time (Böttger, Dingl. polyt. Journ. cxliii. 464). When heat can be applied to the discoloured metal, the silver-sulphide may be decomposed by heating it to redness. The best mode of preventing such discoloration of silver articles when not in use, is to wrap them in paper coated with white lead.

Chlorine, *bromine*, and *iodine* combine with silver, even at the ordinary temperature. *Hydrochloric acid* in solution has but little action on metallic silver, unless it be heated to the boiling-point with the very finely divided metal; the gas is decomposed by silver at a red heat, silver-chloride being formed. Under similar conditions the vapours or other chlorides are decomposed by metallic silver. *Sodium-chloride* ignited with precipitated silver is decomposed, and the silver almost entirely converted into chloride; but when the metal is in large pieces, the formation of silver-chloride is merely superficial, unless the salt is melted, and, by the consequent solution of the chloride, a fresh surface becomes exposed. Silver kept melted under sodium-chloride, gradually decreases in weight, owing to the formation of silver-chloride, and in two or three hours the loss may amount to 2 or 3 per cent. (G. Rose). If alkaline carbonate be mixed with the sodium-chloride, this reaction is prevented. Aqueous solutions of alkaline chlorides gradually react with silver, producing silver-chloride, which dissolves in the form of a double chloride. Solutions of *cupric chloride* and other chlorides convert silver into chloride.

Dilute *sulphuric acid* does not react with silver, but strong sulphuric acid is decomposed when heated with it, yielding silver-sulphate and sulphurous acid gas. *Nitric acid* reacts with silver, even at the ordinary temperature, dissolving it and yielding silver nitrate and nitric oxide. It is the best solvent of silver.

The saline compounds of silver are mostly colourless, except when the electro-negative constituent they contain is coloured. Both the soluble and insoluble compounds of this metal are blackened by sunlight and decomposed, some silver being reduced. Most silver compounds are decomposed, with reduction of the metal, by the action of heat.

Occurrence.—Silver occurs both in the metallic state, and in combination, chiefly with sulphur, also with chlorine, other metals, &c. Ores of other metals frequently contain silver (Malaguti and Durocher, Compt. rend. xxix. 689; Ann. Min.

[4] xvii. 245). It has also been detected in sea-water. (Ann. Ch. Phys. [3] xxvii. 129.)

Native Silver is sometimes crystallised in cubes, octahedrons, and related forms; sometimes in laminated or filamentous masses, and sometimes very minutely disseminated throughout other minerals. It is very rarely pure, containing either gold, copper, or other metals.

Silver-sulphide occurs as silver-glance, sometimes crystallised, but more frequently massive. It has a dark lead-grey colour, and may be cut with a knife. Its specific gravity is 7·196. It contains 87 per cent. silver. Silver-sulphide also occurs in combination with various other metallic sulphides, constituting a great number of minerals, in which the amount of silver varies from 10 to upwards of 60 per cent.

Silver-chloride occurs as horn-silver, both massive and earthy; sometimes crystallised. It has a pearl-grey colour, sometimes passing into lavender; it is translucent, and very soft. Its specific gravity is 5·552.

Among the other silver-compounds which occur as minerals, the *iodide, bromide, selenide, telluride, antimonide, arsenide*, and *mercuride* are met with less abundantly.

Silver-ores occur almost exclusively in lodes traversing gneiss, mica-schist, grauwacke, clayslate, &c. They consist chiefly of metallic silver, silver-sulphide, and its various compounds (silver-chloride, arsenide, and antimonide), associated with lead and copper ores, blende, pyrites, spathic iron, brown hæmatite, earthy carbonates, heavy spar, quartz, &c.

Besides what may be properly called silver-ores, galena and the different varieties of grey copper-ore (*cuivre gris; fahlerz*), often contain such an amount of silver, that, from the greater value of this metal, they must be regarded as ores of silver as much as, or even more than, lead or copper. Such ores frequently contain, in the ton, from 2 to 10 ounces of silver, sometimes upwards of 100 ounces. Pyritic and earthy minerals also frequently contain a small amount of silver, sufficient to render its extraction profitable.

Preparation.—Pure silver is best obtained by decomposing the chloride, the insolubility of which admits of other metals being easily separated from it by washing with dilute acid and water. One of the most convenient methods is to cover the moist freshly precipitated chloride with dilute sulphuric or hydrochloric acid, and then to place upon it pieces of sheet zinc or iron, leaving the whole at rest until the silver is reduced to the metallic state. With zinc the reaction is represented by the equation:

$$2AgCl + Zn = ZnCl^2 + Ag.$$

When the reduction is complete, the spongy silver should be thoroughly washed with dilute acid and boiling water; then dried, and melted with sufficient alkaline carbonate to cover the surface of the metal, and prevent contact with atmospheric air. The chloride may be mixed with about 70 per cent. of chalk and 4 per cent. of carbon, and gradually heated to a sufficient temperature for melting the reduced metal.

PRODUCTION OF SILVER ON THE LARGE SCALE.

Although silver-compounds are generally decomposible without difficulty by heat, with reduction of the metal, the extraction of this metal from its ores is not by any means so simple a matter as might be expected. This is chiefly owing to the circumstance that argentiferous minerals, and even native silver itself, often occur minutely disseminated throughout a matrix of earthy minerals, or intimately mixed with compounds of other metals.

Very rich silver-ores, containing from 90 to 50 per cent. of silver, may be smelted in crucibles with lead or litharge, and proper fluxes for converting the earthy admixtures into slag. Ores containing 40 per cent. and less may be smelted with granulated lead, litharge, or lead-ores in a small blast-furnace, or in a reverberatory furnace with a concave hearth forming a kind of crucible. Metallic iron is sometimes added when the ore contains sulphides. This method is practised to some extent in California and Nevada.

Rich silver-ores are sometimes smelted by adding them in small successive portions to lead which is undergoing cupellation.

Poor argentiferous ores which do not contain any large amount of other easily reducible metals, are smelted with iron pyrites so as to obtain a matt, consisting chiefly of iron-sulphide with some copper- and lead-sulphides, and containing from 40 to 60 ounces of silver in the ton. Such ores often contain pyrites: if they contain too much they must be partially roasted, and earthy ores require pyrites to be added. The proportion of pyrites should be such that the matt produced may amount to from 30 to 50 per cent. of the ore. The following table gives the composition of several products of this kind:—

Composition of Argentiferous Matts.

Analyst	Plattner.	Conrad.				Fritzsche.
Iron	57·333	54·268	57·781	61·041	56·610	65·620
Lead	8·863	6·828	4·996	3·660	5·489	6·460
Copper. . . .	3·273	5·428	4·416	3·326	5·587	4·000
Zinc	1·381	3·633	2·618	0·667	4·774	3·000
Silver	0·151	0·086	0·086	0·065	0·200	0·117
Nickel	0·515	1·101	1·312	0·524	0·525	
Antimony . . .	0·194	0·274	. .	0·583	0·032	
Arsenic . . .	1·243	0·387	0·240			
Sulphur . . .	26·487	27·042	26·702	27·652	22·489	19·963
Silica	. .	. .	. .	. .	2·666	

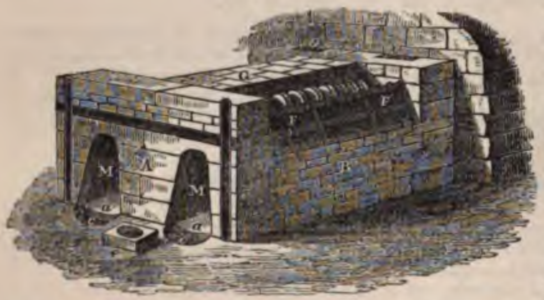
The silver is afterwards extracted from these matts by another operation.

Lead-ores containing silver are smelted in the usual manner (see Lead, iii. 481—526), and the silver is separated from the lead, either by cupellation, or by one of the other methods already described under the head of Lead.

Argentiferous copper-ores are also smelted in the same way as other copper-ores (see Copper, ii. 24—32), and the silver is extracted either from the matt or from the regulus by one of the methods described below.

Separation of Silver from Copper by Eliquation (*liquation; Saigerung*).—This method is based upon the fact that when argentiferous copper is melted with rather more than three times its weight of lead, the silver unites with the lead, and this alloy separates from the copper when the melted metal is gradually cooled. In practice the melted metal is cast into disc-shaped masses, about 2 feet diameter and 3 inches thick, in iron moulds so as to cool it rapidly. A number of these cakes are placed side by side on their edges in the eliquation-hearth (*aire de liquation; Saigerheerd*), *fig.* 744, which has two long cast-iron plates fixed above the open space M, and at a little distance apart. The cakes of metal are laid upon these plates, covered with iron plates (FF) and charcoal, and heated for some time to the melting point of lead. The alloy of lead and silver is thus melted, and gradually flows away through the opening between the plates from the copper, which requires a much higher temperature for melting, and remains behind as a porous mass. The argentiferous lead falls into a gutter (*a*) on the floor of the open space M, and collects in the well *c*. It is afterwards submitted to cupellation to separate the silver.

Fig. 744.



The amount of silver in the copper to be treated by this method must not be less than from 80 to 90 ounces per ton, nor more than 200 ounces per ton. A smaller amount of silver would not repay the cost of the operation, and a larger amount would be only partially separated from the copper. The proportion of lead should not be less than from 30 to 32 lbs. to the ounce of silver.

This method is very imperfect, since the copper always retains from 10 to 20 per cent. of silver, and a number of bye-products are formed containing lead, copper, and silver, which require further treatment.

Extraction of Silver by Amalgamation.

The extraction of silver from its ores and from argentiferous products of other metallurgical operations, is very frequently effected by a method based upon the easy solubility of silver in mercury. This method was invented in Mexico by Bartolomeo de Medina about the year 1557; and being specially suited to that country, by reason of its requiring very little fuel, it soon came into general use, and is now extensively practised, with various modifications and improvements, in all the silver-producing countries of the Western Continent.

The amalgamation of silver-ores differs from the amalgamation of gold-ores, which contain gold in the metallic state, in requiring a preliminary treatment of the ores for the purpose of bringing the silver they contain into such a condition that it can be dissolved by mercury. Silver-ores contain not only metallic silver, but silver-sulphide and other compounds which are not acted upon by mercury. Silver-chloride, however, is decomposed by mercury with formation of mercurous chloride:

$$\mathrm{AgCl + Hg = HgCl + Ag.}$$

Consequently the first step in the operation is to convert all the silver-compounds into chloride.

1. *Mexican method.*—In the treatment of silver-ores by this method, silver-chloride is produced in the wet way by the reaction of cupric and ferric or ferrous salts with silver-sulphide, in the presence of sodium-chloride in excess. The precise nature of the reactions which take place is not well understood. When silver-sulphide is digested with solution of cupric or ferric chloride, no reaction takes place; but when it is mixed with cupric sulphate or ferrous sulphate and sodium-chloride in the moist state, some silver-chloride is formed after a time (Karsten). A solution of cupric chloride with excess of sodium-chloride, digested with silver-sulphide for some days at the ordinary temperature, is gradually decolorised, and the products of the reaction are cupric sulphide with silver-chloride and cuprous chloride, which are partly dissolved by the excess of sodium-chloride. Sulphur is also said to be separated (Boussingault). In this case the reaction is probably as follows:

$$\overset{648}{\mathrm{3Ag^2S}} + \overset{256\,''}{\mathrm{4CuCl^2}} = \overset{648}{\mathrm{6AgCl}} + \overset{128}{\mathrm{2CuCl}} + \overset{128\,''}{\mathrm{2CuS}} + \overset{32}{\mathrm{S}}.$$

The cuprous chloride produced would, in the presence of sodium-chloride, be capable of converting a further quantity of silver-sulphide into chloride as follows, being itself converted into cuprous sulphide:

$$\overset{216}{\mathrm{Ag^2S}} + \overset{128}{\mathrm{2CuCl}} = \overset{216}{\mathrm{2AgCl}} + \overset{128}{\mathrm{Cu^2S}}.$$

The production of cuprous chloride may also be determined by the presence of metallic silver in the ore by the following reaction:

$$\overset{''}{\mathrm{Cu}}\mathrm{Cl^2 + Ag = AgCl + CuCl.}$$

Heat facilitates the production of chloride, and the silver-sulphide is more readily converted into chloride when it is combined with antimonial sulphide.

In order to submit the ores to this preliminary treatment, they are ground very fine with water in a mill resembling a porcelain mill. The sludgy mass is laid out on a paved floor in heaps called *torta* or *montone*, upon which from 1 to 5 per cent. of common salt is sprinkled, and the whole well stirred together either with shovels or by treading under the feet of mules. Some days afterwards it is mixed with from 0·5 to 1 per cent. of *magistral*, consisting essentially of cupric and ferrous or ferric sulphates, and prepared by roasting cuprous pyrites. Sometimes roasted iron-pyrites is used, but a magistral containing copper is preferred. At this stage of the process chemical action takes place; part of the sodium-chloride, reacting with the sulphates of the magistral, yields sodium-sulphate, with cupric and ferric or ferrous chlorides, which give rise to the formation of silver-chloride as above described.

The decomposition of the silver-chloride is effected by means of mercury. The quantity employed for this purpose and for the actual amalgamation of the silver generally amounts to about six times the weight of the silver in the ore. It is added in three equal portions at intervals of 15 or 20 days, and is thoroughly incorporated with the mass of ore. The day after the first portion of mercury has been added, the mass is tested by washing a portion of it with water, to ascertain from the appearance of the amalgam whether the process is going on properly. It is essential to the success of the operation that there should not be any cupric chloride remaining when the mercury is added to the heap, because the reaction which would take place between it and the mercury, resulting in production of mercurous chloride, would unnecessarily augment the waste of mercury. If the mercury appears very grey and much subdivided, too much magistral has been used, and consequently the mass contains a large amount of mercurous chloride: in that case chalk is added. If, on the contrary, the mercury is very brilliant and liquid, there is not enough magistral, and more has to be added. When the mercury separated in the test presents a slightly grey dull appearance, and runs together rapidly when separated into globules, the process is going on well.

About fifteen days after the first portion of mercury has been added, it will have combined with enough silver to form a pasty amalgam; then a further quantity is added, and after another interval of rest, the third portion is added. This operation lasts altogether two or three months, according to the nature of the ore, the temperature, &c. If the amalgam is pasty at the end of the operation, a further quantity of mercury is added to liquefy it, and the whole mass is washed with water in large wooden vats fitted with paddles on vertical shafts. The amalgam thus separated is pressed in sacks to strain off excess of mercury, and then distilled.

At some places this method of treatment is practised without the use of magistral, and merely with salt and mercury. In those instances it is probable that the ores contain sufficient sulphides for the production of cupric or ferrous sulphates by the action of atmospheric oxygen during the mechanical preparation of the ore.

The ores worked in this way in South America and Mexico are generally sorted, so as to contain from 20 to 40 ounces of silver to the ton, the richer parts being picked out and smelted.

The consumption of mercury in decomposing silver-chloride, and the waste attending the several operations, are said to amount, in the Mexican method, to about twice the weight of the silver obtained. It has been proposed to recover the mercury left in the washed residue as mercurous chloride by treating it with hypochlorite of calcium or nitrate of sodium, and then adding excess of hydrochloric acid so as to convert the mercurous chloride into mercuric chloride, which could be washed out, and the mercury precipitated by copper, while the solution of cupric chloride thus obtained would serve in the place of magistral for subsequent working.

Since the decomposition of silver-chloride may be effected in the wet way by contact with other metals besides mercury, the consumption of mercury in that way might be prevented. With this object De Lecca proposed, in 1586, to modify the treatment by using iron plates together with the mercury, but this suggestion was little regarded at the time.

For the amalgamation of rich ores, **Alonso Barba** devised a method with the same object, which consisted in grinding the ores in copper pans with successive additions of salt, magistral, and mercury. The silver-chloride being in this case decomposed by copper, less mercury was requisite; but the extraction of the silver was incomplete.

2. *European Amalgamation.*—The method of extracting silver from its ores by means of mercury was made known in Europe about the middle of the seventeenth century, and Barba's modification of it was the starting-point from which it came to be adopted. The first attempts to work silver-ores by amalgamation were made in the Austrian States by v. **Born**, and after successive improvements, works were also erected at Freiberg, Neusohl, and other places on the Continent, where it was extensively practised.

The principal points of difference from the Mexican method are:—1. The conversion of the silver-compounds in the ore into chloride by treatment in the dry way by roasting with salt; 2. The decomposition of the silver-chloride by copper or iron instead of mercury.

The silver ores which are treated by amalgamation in Saxony contain silver-sulphide combined or mixed with arsenical and antimonial sulphides, pyrites, blende, &c. Both rich and poor ores can be worked by this method with equal advantage; but since the proportion of salt and mercury to be used would depend upon the amount of silver in the ores, and since this varies from 20 to 500 ounces per ton, the ore is sorted, so that the mass to be operated upon may contain from 60 to 70 ounces of silver per ton, and a uniform mode of treatment may be adopted.

It is necessary that the ore should contain sulphides in sufficient amount to produce the requisite chemical reactions during the roasting, and to ascertain whether this is the case, a portion is melted with glass, borax, and resin in an assay-crucible under a cover of sodium-chloride. It should yield about 30 per cent. of matt. When there is a deficiency of sulphides, iron-pyrites or ferrous sulphate is to be mixed with the ore.

In the preparatory treatment, the finely-ground ore is roasted with 10 or 12 per cent. of common salt in a reverberatory furnace. The charge is put into the furnace moist, gently heated at first, and stirred continually until it is dry, so as to prevent its caking; it is then raked up into a heap along the hearth, and after the lumps have been broken, it is spread out evenly, and stirred about while the heat is being increased to redness. This stage of the operation (*Anfeuern*) generally occupies about two hours. Meanwhile steam and some vapours of arsenic and antimony are given off. As the temperature rises to redness, the sulphides begin to be decomposed by reacting with atmospheric oxygen, and then the combustion of the sulphur generates so much heat that no fresh fuel is required to keep up the temperature during this stage of the process (*Abschwefeln*), which also lasts about two hours. The disengagement of sulphurous acid, together with arsenic and antimonial vapours, causes the mass to become pulverulent and porous, and when it ceases the temperature begins to fall. The heat is then raised considerably, for the purpose of decomposing the sulphates which have been produced. A fresh evolution of sulphurous acid together with chloride-vapours then begins, causing the mass to swell up. During this stage of the process (*Gutrösten*) the sulphates react with part of the sodium-chloride, yielding sodium-sulphate, ferric chloride, &c., while some hydrochloric acid and chlorine are disengaged, and the silver is converted into chloride. Care must be taken not to continue this part of the operation too long, since the silver-chloride might be melted or decomposed, and thus the efficiency of the subsequent operations would be interfered with, and the yield of silver consequently reduced. After about an hour, the charge is drawn from the hearth. It then contains, besides various oxides and the earthy ingredients of the ore, silver-chloride, cupric and ferric chlorides and sulphates, sodium-chloride and sodium-sulphate, and some unaltered sulphides.

During the roasting, the charge loses about 10 per cent. by weight, and some silver is carried away in the vapour given off, for which reason the smoke is passed through soot-chambers and condensers. The flue-dust thus deposited contains unaltered particles of ore, with carbon, various saline substances, and about 30 or 40 ounces of silver per ton. This silver is often in the state of antimoniate, a salt which is always produced when argentiferous and antimonial minerals are roasted together (Plattner). The formation of this salt causes a further loss of silver, from the fact that it is not convertible into chloride by means of chlorine, but only by hydrochloric acid.

The roasted ore is screened and sifted from the lumps, which are ground and roasted again with salt. The fine powder is ground in a mill, and passed through a bolting-cloth to reduce it to an extremely fine state of division. This mechanical treatment is of great importance for the perfect separation of the silver by treatment with mercury.

The decomposition of the silver-chloride (*Anquicken*) is generally effected by stirring the roasted ore with water and iron or copper in strong wooden casks mounted horizontally in a framework, and made to revolve by machinery:

$$\overset{216}{2AgCl} + \overset{56}{Fe} = Fe''Cl^2 + Ag; \text{ or } \overset{108}{AgCl} + \overset{64}{Cu} = CuCl + Ag.$$

This reaction is greatly facilitated by the presence of an acid, and when two metals act simultaneously, it takes place more rapidly than when only one is present. In this case the more electro-positive metal is converted into chlorine by the reduction of the silver. Thus when copper and mercury are used together, mercurous chloride only is produced. With iron and mercury, on the contrary, only ferrous chloride is produced, together with silver-amalgam.

The stirring with metallic iron or copper has also the effect of converting ferric chloride into ferrous chloride. Cupric chloride is decomposed in the same way, and unnecessary production of mercurous chloride is thus prevented.

The quantity of iron consumed in this process is more than equivalent to the silver-chloride decomposed, and amounts to about 60 per cent. of the silver obtained: the excess being partly due to the solvent action of salts in the roasted ore, and partly to the precipitation of other metals besides silver.

When copper is used instead of iron, a much purer amalgam is obtained; but copper acts more slowly, and even when used in large proportion, it is not so effective as iron in extracting the silver.

The decomposition of silver-chloride by either iron or copper is also much facilitated by the presence of alkaline chlorides, especially when the solution is strong. This is most probably owing to the solubility of silver-chloride in such solutions, and to the consequently increased chemical action. This silver-chloride is reduced more rapidly by mercury, in the presence of a concentrated solution of alkaline chloride, than it is by either iron or zinc alone.

After this operation has been completed, and the silver has been reduced to the metallic state, a quantity of mercury, equal to about half the weight of the roasted ore, is put into each cask, and the stirring is continued again for about twenty hours. During this operation the contents of the cask are examined from time to time, to ascertain whether the proper quantity of water has been added, and to test the condition of the charge.

The casks are next filled with water and made to revolve slowly for about two hours, after which time the greater part of the amalgam will have separated from the sludgy mass and collected together, so that it can be drawn from the casks. It is filtered through canvas bags to separate excess of mercury, and distilled in iron retorts.

The pressed amalgam contains about 85 per cent. of mercury, and from 10 to 12 per cent. silver, with varying amounts of copper, lead, antimony, &c. The strained mercury contains about one ounce of silver in the hundredweight.

The sludgy mass (*tailings*) remaining in the amalgamating casks still contains disseminated particles of amalgam and mercury. It is run into a wash-tun (*agitator, Waschbottige, cuve*), mixed with a large quantity of water and stirred with paddles. The amalgam which collects at the bottom of the agitator is much more impure than that taken direct from the casks. The lighter portion of the tailings is run off from side-openings at different levels of the agitator, and the heavier portion is again treated with mercury in the casks, or dried, ignited, and used in the smelting-works. It sometimes contains 140 ounces of silver per ton. The finer portion of the tailings also contains some silver, from 2 to 5 ounces per ton.

The mother-liquor from the tailings contains sodium-chloride and sulphate, with other salts, such as ferrous and manganous sulphates, small quantities of phosphates, arsenates, and fluorides, &c. It is concentrated in leaden pans, or frozen in winter to obtain the sodium-sulphate.

The loss of silver and mercury in this operation is subject to great variation; the former amounts to about 5 or 10 per cent. of the quantity contained in the ore. Of this from 2 to 4 per cent. is either volatilised in the roasting, or lost in the grinding and sifting of the ore, and in melting the metal. From 3 to 5 per cent. of the silver generally remains in the tailings. A small portion of the mercury is converted into mercurous chloride, which is not decomposible by iron. Much more remains mechanically disseminated among the tailings, and is washed away in the mother-liquor. The presence of lead, arsenic, and other metals, which are easily reduced and amalgamated, augments considerably the waste of mercury. At Freiberg it amounts to about fifteen ounces per ton of ore, and 87 per cent. of that is washed away in the mother-liquors, or remains in the tailings.

The advantages of the amalgamation method over smelting, consist in the smaller loss of silver, the greater simplicity of the operations, the more rapid extraction of the metal, saving in fuel, and the absence of injurious vapours. On the other hand, it is not applicable to ores containing lead or copper. Although lead amalgamates very readily when in the metallic state, still in the treatment of ores containing lead, only a small part of this metal is amalgamated. This is probably because very little of the lead is reduced, the greater part remaining in the state of chloride or sulphate, which are not decomposed unless there is a very large excess of iron in the amalgamating casks. Copper is partly taken up by the mercury, and part remains in the tailings. If these are not sufficiently rich to be worked, that portion of the copper is lost. Consequently, ores containing more than 7 per cent of lead or 1 per cent. of copper are not treated by the amalgamation method.

Auriferous silver-ores likewise cannot be advantageously worked by this method, because the greater part of the gold remains in the tailings after amalgamation, and is lost. Comparative trials have shown that silver obtained from such ores by smelting, contained more than twice as much gold as that obtained by amalgamation. The reason of this is, that though gold amalgamates very readily with mercury, still in the treatment of silver-ores by this method, it is less rapidly acted upon than the silver, which is reduced from the silver-chloride in a finely-divided spongy state, favourable to its amalgamation.

The nature of the earthy ingredients of the ore has also some influence on the working: thus clay renders the mass tenacious in the amalgamation; heavy spar makes it dense; calcareous substances reduce the consumption of iron and of mercury by decomposing the chlorides, but they also lessen the yield of silver. In this respect a judicious admixture of quartzose and calcareous ores is most advantageous.

The method of amalgamation is applied not only to silver-ores but also to the matt (*Kupferstein*) and the coarse copper (*Schwartzkupfer*) obtained in smelting argentiferous copper-ores. (See COPPER, ii. 31.)

In the Mansfield district, silver was formerly extracted in this way from copper-matt, after it had been roasted with salt to convert the silver into chloride. The tailings were afterwards smelted with quartz, fluor-spar, and slag to obtain the copper.

At Schmöllnitz, in Hungary, black copper, containing from 85 to 89 per cent of copper, and 200 or 300 ounces of silver per ton, is worked by amalgamation. The metal is reduced to powder by stamping while red-hot and then grinding. It is mixed with from 7 to 9 per cent. of salt, and roasted in a reverberatory furnace. The amount of sulphur in the metal, being no more than from 0·5 to 1 per cent., would be insufficient in this case to determine evolution of chlorine by its oxidation to sulphuric acid; consequently the production of silver-chloride in the roasting must be effected chiefly by the reaction of sodium-chloride with the metal.

The silver-chloride is decomposed by means of copper, and the amalgamation otherwise conducted as already described (p. 282). If iron were used instead of copper to decompose the chloride, the metal obtained would contain a large amount of copper.

The loss of silver is said to be less than 5 per cent., and the waste of copper about 2 per cent. The waste of mercury, however, amounts to 40 ounces per ton of coarse copper.

At Cziklowa, in the Bannat, coarse copper containing 16 ounces of silver per ton is roasted with 10 per cent. of salt and 3 or 4 per cent. of pyrites.

At Offenbanya, in Transylvania, coarse copper containing 10 per cent of lead is roasted for six hours with 18 per cent. of salt and 3 per cent. of nitre, to facilitate the production of lead-sulphate, which is not decomposed in the amalgamation.

The compound of arsenic and antimony with nickel, cobalt, iron, and other metals, which is termed *speis*, produced in lead-smelting, and especially in the preparation of smalt from nickeliferous cobalt-ores, often contains silver which is extracted by amalgamation.

The speis from the Saxon smaltworks at Schneeberg contains from 10 to 100 ounces of silver per ton. It also contains bismuth and sulphur. The powdered material is roasted to oxidise the metals: part of the arsenic is volatilised as arsenious acid; a great part, however, remains in the state of arsenic acid combined with the basic oxides. The roasted product is sifted, to separate any melted or unoxidised particles, then ground fine, mixed with 8 per cent. of salt and 2 per cent. of ferrous sulphate, and again roasted to convert the silver into chloride. More arsenious acid is volatilised, and probably some arsenic as chloride. The product of this roasting is ground very fine, and treated with mercury in casks.

The amalgam requires to be well washed with water to remove bismuth-oxide. The tailings contain 5 ounces of silver per ton, and are smelted for nickel. The total loss of silver is said to be about 15 per cent.; the waste of mercury amounts to 10 or 15 ounces per ton.

At Poullaouen, in Brittany, some of the ores from the Huelgoet mines, consisting of metallic silver, antimonial silver, and silver-chloride disseminated through quartz, ochre, and clay, are treated in a manner which combines both the Mexican and European methods. After the mechanical preparation of the ore, containing about 20 ounces of silver per ton, it is mixed with water and 10 per cent. of magistral, consisting chiefly of sodium-chloride, with some ferrous sulphate, alum, and a very small amount of cupric sulphate. This mixture is left for about 15 days in tubs, to allow of the production of silver-chloride, and the subsequent treatment conducted as already described.

The extraction of silver is effected to within 3 ounces to the ton.

The waste of mercury amounts to from 10 to 80 ounces per ton of ore.

The amalgamation method is now largely practised in California and Nevada in working silver-ores, and great improvements have been made in connection with it. Iron pans with mullers, for grinding the ore either in the raw or roasted state, have been substituted for the barrels with great advantage. By this means the silver or silver-compounds of the ore are more effectively brought in contact with the chemicals and mercury, and the amalgamation is much facilitated. The application of heat by steam-pipes has also been found very advantageous.

One of the most troublesome circumstances connected with the extraction of silver by amalgamation is the conversion of the mercury into a pulverulent condition, known as "flouring," when it is liable to be washed away in the tailings, together with silver it has combined with. Considerable loss may be caused in this way; and as this effect is due to the combination of sulphur, oxygen, &c. with a portion of the mercury, it has been proposed to introduce a small amount of sodium into the mercury used for amalgamation. From the great chemical affinity of this metal for sulphur and oxygen, it prevents the mercury from becoming "floured," and materially reduces the waste of this metal and the loss of silver. An amalgam containing about 30 per cent. of sodium is used for the purpose, and added to the mercury so as to make the proportion of sodium about 1 or 2 per cent. The presence of sodium in the mercury also appears to facilitate very considerably the amalgamation of the silver. (See Crooke's Specifications, Nos. 391 and 2229, dated 11th February and 30th August, 1865.)

The use of caustic alkali for the same purpose has also been tried and found advantageous, though probably in a less degree than the sodium-amalgam.

Extraction of Silver as Chloride and Sulphate.

The solubility of silver-chloride in a strong solution of sodium-chloride has been taken advantage of for the purpose of extracting silver from copper matts and ores without the aid of mercury. The silver is converted into chloride by roasting with salt, and the roasted product is digested with a concentrated solution of salt in wooden vats. The silver-solution is drawn off and passed through a series of vats containing precipitated copper, which separates the silver, while a solution of copper is produced, from which the copper is recovered in a state fit to be used again, by passing through another series of vats containing iron. The liquor from which the copper has been precipitated, is left for some time exposed to the air, till a great part of the iron has been deposited as a basic ferric salt; it then contains some sodium-sulphate produced in the roasting, and is either evaporated to obtain that salt, or treated with calcium-chloride to furnish sodium-chloride for future use. (Augustin.)

A still more simple and inexpensive method of extracting silver is based upon the facts that silver-sulphate is soluble in water, and that it requires a higher temperature for decomposition than any of the other soluble sulphates containing heavy metals which are produced during the roasting of copper-matt or of silver-ores with pyrites. The success of this method of treatment depends mainly on the proper roasting of the material from which silver has to be extracted, so that the whole of the silver may be obtained in the state of sulphate, while the cupric and ferrous or ferric sulphates are decomposed. In the roasting the heat is to be gradually raised during the space of three or four hours to dull redness, and lastly increased within about two hours to cherry-red. The progress of the roasting is ascertained from time to time by testing a portion of the charge with water. It should give a faintly bluish solution, and the amount of silver rendered soluble may be estimated volumetrically with a salt-solution of known value. When the proper condition has been reached, the charge is drawn from the furnace and digested with water, and the silver is precipitated from the solution by copper. (Ziervogel.)

The average loss of silver by this method is said to be only 8 per cent.

The use of alkaline hyposulphite has been proposed as a solvent for silver-chloride in the working of ores, &c., the silver being precipitated from the solution as silver-sulphide by means of alkaline sulphide, while a solution of hyposulphite is reproduced. (Percy.)

In the case of very poor argentiferous materials, such as the residue from the burning of pyrites in the manufacture of sulphuric acid, it has been proposed to volatilise the silver as chloride, and collect it in condensers.

When the silver obtained by this method is very impure, it is sometimes purified by cupellation with lead. Attempts have been made to separate the metals with which the silver is alloyed, by digesting with dilute sulphuric acid in leaden pans, the residue left by distillation after it has been heated to redness in contact with atmospheric air. By repeating this treatment several times, a large portion of the foreign metals are separated, but the purification is incomplete and the cost is considerable. More frequently the silver is refined by melting in cast-iron crucibles. By this means the foreign metals are oxidised and form a slag, which floats on the surface of the melted silver and is skimmed off. Some charcoal-powder is then sprinkled on the metal, the crucible covered, and the heat kept up for a time, the metal being stirred in the meanwhile with an iron rod. When the charcoal is consumed, this operation is repeated until the metal exhibits the required degree of purity. It is then cast into ingots. This refined metal ought not to contain less than 70 per cent. silver, and the alloy should consist entirely of copper.

The refuse of the refining is melted with potash and some nitre under sodium-chloride, and a silver regulus is obtained, together with a rich matt, which is mixed with the ore for amalgamation, and a slag which is sent to the smelting-works. B. H. P.

SILVER ALLOYS. For most of the useful purposes to which silver is applied, the pure metal would be too soft to resist sufficiently the wearing-away of the surface by friction. The presence of a small amount of copper in the metal very considerably increases its hardness, without much affecting the colour, and consequently silver is generally used in the state of an alloy with copper.

Silver may be alloyed with most other metals. None of the alloys are so soft and ductile as pure silver, though generally more so than the metal with which it is alloyed. The presence of small quantities of other metals—such as antimony, arsenic, bismuth, tin, and zinc—renders silver brittle and liable to crack when rolled, but to a less extent than is the case with gold or even with copper.

1. With Aluminium.—The alloys of these metals are much harder than pure aluminium, and when the aluminium amounts to twice as much as the silver, they are even more fusible than aluminium, and may therefore be used for soldering that metal. The alloy containing 3 per cent. of silver is not acted upon by sulphuretted hydrogen: that containing 5 per cent. of silver has a fine white colour, takes a good polish, has about the same degree of hardness as British standard-silver, and is tolerably malleable. Equal parts of aluminium and silver give a brittle alloy.

2. With Antimony.—A very small proportion of antimony alloyed with silver is sufficient to render the metal liable to crack in rolling. Alloys of silver and antimony occur as minerals.

3. With Bismuth.—Equal parts of silver and bismuth form a crystalline brittle alloy, of 10·709 specific gravity. Bismuth-oxide being fusible, this metal can be separated from silver by cupellation in the same way as lead.

4. With Copper.—Silver and copper may be melted together in any proportion. The alloys are almost as ductile as silver; and they have much greater hardness and elasticity, and are capable of taking a much higher polish than pure silver. Those containing less than half their weight of silver are white.

The most important alloys of silver and copper are those employed for coinage, and for the manufacture of silver utensils and ornaments, &c. The standard value of the alloy used for these purposes varies in different countries. In England "*standard silver*" contains 7·5 per cent. copper: its specific gravity is 10·20.

In France there are three standard alloys: one, containing 95 per cent. of silver, for medals and plate; the second, containing 90 per cent., for coin; and the third, containing 80 per cent., for jewelry-work.

In Germany and Austria there are two standards for coin, of different values—one containing 90 per cent., the other 87·5 per cent. silver. The alloy used for silver-plate varies from 70 to 81 per cent.

Silver-solder contains about 66 per cent. silver with zinc and copper.

When alloys of silver and copper solidify gradually, they do not remain homogeneous throughout. According to the amount of silver they contain, the inner or outer portions of the mass contain a larger proportion of silver than the remainder. Levol states that this separation does not take place with the alloy consisting of 71·9 per cent. silver and 28·1 copper. (Ann. Ch. Phys. [3] xxxvi. 220.)

Although the alloys of silver with copper are white, even when containing a large amount of copper, still the colour is not so fine as that of pure silver. Such alloys, after being manufactured, are therefore submitted to an operation by which the copper is superficially oxidised, and dissolved out, so as to leave a film of pure silver. This is termed *whitening* (*blanchiment; Ansieden*).

5. With Gold. This metal may be alloyed with silver in all proportions. Levol regards the alloys of these metals in equivalent proportions as being incapable of separating by gradual cooling. (Ann. Ch. Phys. [3] xxxix. 163.)

Alloys of gold and silver in various proportions occur native. (G. Rose, Pogg. Ann. xxiii. 161.—Awdejew, *ibid.* liii. 153.—Boussingault, Ann. Ch. Phys. [2] xxxiv. 408; xlv. 440.—*Gmelin's Handbook*, vi. 247.)

6. With Lead.—Silver may be melted with lead in all proportions. These alloys when slowly cooled, separate, so that the interior of the mass contains a much larger proportion of silver than the outside. (Levol, Ann. Ch. Phys. [3] xxxix. 163.)

7. With Mercury.—This metal combines with silver at the ordinary temperature, forming one of the soft alloys called amalgams, which mixes with an excess of mercury, but may be separated as a pasty mass by squeezing in wash-leather. Silver-amalgam occurs native, sometimes crystallised (iii. 889).

8. With Nickel.—The alloy containing 13·4 per cent. of nickel, is greyish-white, and takes a good polish. It is highly magnetic. The alloy used for coin in Switzerland contains 10 per cent. of nickel. It is very hard, and not so white as the alloys commonly used for coin.

9. With Platinum.—Alloys of silver with platinum are much less ductile than pure silver. The alloy containing 64·3 per cent. platinum, has a colour intermediate between those of the two metals. It cannot be rolled without cracking. Silver containing only 0·07 of platinum is very brittle, and cannot be cupelled; even as little as 0·05 greatly impedes the cupellation. Sulphuric acid dissolves the silver from these alloys. Nitric acid dissolves part or all of the platinum as well as the silver, according to the proportion of the two metals.

10. With Tin.—Alloys of this metal with silver are nearly as white as pure silver. They are brittle and generally hard, that containing 20 per cent. of tin being about as hard as bronze.

11. With Zinc.—These alloys are of a bluish-white colour. Döppler's reflector metal consists of 80 pts. silver and 20 pts. zinc.

SILVER ASSAY. The estimation of the amount of silver in coin, alloys, ores, &c., for practical purposes. This operation may be conducted either in the wet way, by precipitating the silver as chloride from the solution of a known weight of the substance to be assayed (see SILVER, DETECTION AND ESTIMATION OF, p. 298), or in the dry way by cupellation with lead, so as to obtain the pure silver.

In operating upon ores containing metallic silver and oxidised silver-compounds, they are mixed with eight or ten times as much litharge, and twice as much black flux, and melted in earthen crucibles. The lead reduced by the carbon of the black flux dissolves the silver, and collects as a button at the bottom of the crucible, while the remainder of the litharge and the alkaline carbonate combine with the silicious and earthy ingredients of the ore, forming a slag.

Ores containing sulphur or arsenic may be melted with litharge alone in sufficient proportion to oxidise those substances, and the lead reduced at the same time will be sufficient to dissolve the silver. If the amount of sulphide should be very large in proportion to the silver, it is better to separate some of the sulphur by roasting the ore, or to oxidise it by melting it with nitre before the treatment with litharge.

Argentiferous galena may be assayed by melting it with one-and-a-half times its weight of black flux, and about one-fourth its weight of small iron nails, to obtain a button of metal. Or it may be melted with three or four-tenths of its weight of nitre, which oxidises the sulphur, forming potassium-sulphate, while the lead and silver are reduced. The addition of sodium-carbonate or litharge as a flux is often necessary and convenient in moderating the reaction between the nitre and sulphides.

The button of metal obtained by any of these operations consists of an alloy of silver and lead. The separation of these metals is effected by *cupellation* (*coupellation; Abtreiben*). This operation is founded on the fact that when such an alloy is melted and exposed to a current of atmospheric air, the lead is oxidised, while the silver remains unaltered. The separation of the lead is facilitated by melting the alloy upon a *cupel* (*coupelle; Capelle*), made of bone-earth powder compressed so as to be sufficiently porous to absorb about its own weight of melted lead-oxide, which is thus removed from the metal as the oxidation advances, until at last there remains only the pure silver.

In the assay of argentiferous copper-ores, the first step is to obtain a button containing the entire quantity of both metals. For this purpose ores which do not contain sulphur, arsenic, or antimony, but consist chiefly of oxygen-compounds of copper with earthy admixtures, may be melted at once with black flux sufficient to reduce the metal, and with a flux to convert the earthy ingredients into liquid slag. Borax or litharge may be used as the flux, care being taken to avoid, in the one case, loss by intumescence, and, in the other, the reduction of much lead in proportion to the silver and copper.

Argentiferous copper-ores containing sulphides must be first roasted by gradually heating the powdered ore in a shallow capsule, until sulphurous acid is no longer given off. Great care must be taken at first to prevent any partial fusion of the ore, and, when arsenic is present, it must be very slowly volatilised—otherwise the vapour may carry away some silver. After the ore is fully oxidised, the heat is to be raised sufficiently to decompose the sulphates produced. The roasted ore may then be melted with three or four times its weight of black flux. The button of copper and silver thus obtained is cupelled with lead, to separate the copper from the silver, and the silver is weighed.

1. *Silver Assay in the dry way: Cupellation.*—The assay of alloys of silver and copper by cupellation is of considerable practical importance. When such alloys are melted in contact with atmospheric air, the copper is oxidised, as in the case of an alloy of silver and lead: but the copper-oxide being infusible at the temperature, it cannot be absorbed by the cupel, and its separation requires a solvent. For this reason lead is added in the cupellation of silver alloys containing copper: it serves a twofold purpose—facilitating the fusion of the alloy by acting the part of a solvent to it at a temperature much below the melting-point of either silver or copper, while the oxide it yields during the cupellation melts, and dissolves the copper-oxide produced at the same time.

Karsten's Table (p. 289).

Lead.	Copper.	Copper remaining after Cupellation.	Absorbed as Oxides by the Cupel.	
			Lead.	Copper.
100	100	78·75	5·00	1
200	100	70·12	7·10	1
300	100	60·12	7·70	1
400	100	49·40	7·90	1
500	100	38·75	8·10	1
600	100	26·25	8·15	1
700	100	19·75	8·00	1
800	100	8·75	8·70	1
900	100	5·62	9·50	1
1000	100	1·25	10·10	1
1050	100	0·	10·50	1

The amount of copper capable of being dissolved in this way by lead-oxide, so as to be absorbed by the cupel, varies according to the temperature. The relative proportions of copper and lead absorbed as oxides by the cupel also vary, even at the same temperature, according to the proportion of these metals in the alloy. Karsten, by cupelling copper with different proportions of lead at one and the same temperature, obtained the results given in the preceding table.

Besides these total differences, the proportion of copper-oxide dissolved when an alloy of lead with excess of copper is cupelled, varies throughout the operation. At the commencement it amounts to only 0·13 of the lead-oxide, and at the end to 0·36, or more than a third. When the proportion of lead to copper is too small, the melted oxides are not sufficiently liquid, at the temperature proper for cupellation, to be readily absorbed by the cupel. In this case the oxide accumulates above the metal, and eventually stops the oxidation. The assay is then said to be *chilled* (*noyé; ersaufen*). Therefore, in order to separate the whole of the copper from an alloy of silver with this metal, it is necessary to use enough lead. The complete separation would always be effected with any alloy by using the maximum proportion of lead, or as much as would be necessary with pure copper. But, since this operation is always attended with a loss of silver, which increases in proportion to the time it lasts, and to the amount of metal oxidised, it is indispensable to render this loss as small as possible. For that reason only so much lead is to be used as may be actually necessary, according to the amount of copper in the alloy to be assayed.

The proportion of lead requisite for effecting the separation of copper from silver by cupellation is to some extent influenced by the amount of silver in the alloy. Experience has shown that, in cupellation, copper is less readily oxidised when it is alloyed with silver than when pure; and that, consequently, a larger proportion of lead must be used, relatively to the copper, the greater the amount of silver in the alloy.

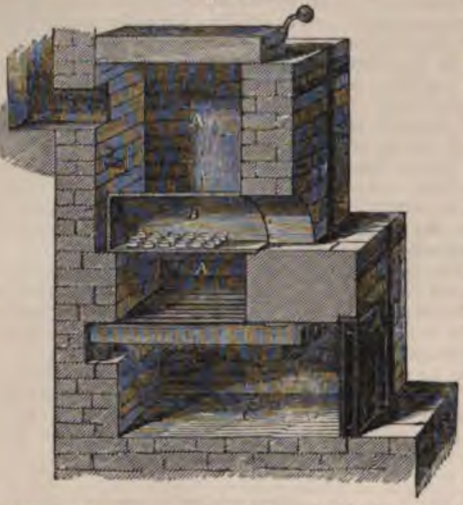
Composition of Alloy.		Quantity of Lead for 1 part of Alloy.	Ratio.	
Silver.	Copper.		Lead.	Copper.
1000		0·3		
	50	3	60	1
900	100	7	70	1
800	200	10	50	1
700	300	12	40	1
600	400	14	35	1
500	500		32	1
400	600	16—17	27	1
300	700		23	1
200	800		20	1
100	900		18	1
	1000		16	1

It is remarkable that when the copper amounts to more than one-half of the alloy, the same proportion of lead is necessary for all alloys, whatever may be the amount of copper they contain. Even when pure silver is melted on a cupel, a little lead must be added to make the metal form a button; if less than three-tenths its weight of lead is used, the button is not properly formed, and the lead is not separated unless the heat be raised considerably, which causes great loss of silver. When, on the contrary, more than that proportion of lead is used, the cupellation takes place readily, but the loss of silver is greater, because the operation lasts longer.

The furnace in which cupellation-assays are made is represented in *fig.* 745. The most important part of it is the *muffle*, B. This is a semicylindrical vessel made of clay, and closed at one end. It is fixed in the furnace in such a manner that it can be entirely surrounded with the burning fuel when the furnace is in use. At the sides of the muffle there are longitudinal openings, through which a draught is produced by the chimney; and when the door of the muffle is opened, a current of atmospheric air is thus made to pass through the muffle over the cupels.

In using this furnace, it should be kept entirely filled with fuel which will burn without smoke; and when the temperature has been raised to the proper degree, it can easily be regulated according to requirement. When the cupels have become hot, and the sides of the muffle are at a bright red heat, verging upon white, the necessary quantity of lead is first placed in the several cupels; and when it is melted, the weighed quantities of the alloys to be assayed, wrapped in thin paper, are quickly but gently slipped into the melted lead, great care being taken to prevent any portion of the contents of the cupels being thrown out.

Fig. 745.



After the cupels are charged, the muffle is closed for a few seconds, that the pieces of alloy may melt and dissolve in the lead. At the moment the door is removed, the contents of each cupel should present the appearance of bright liquid metal with a convex surface.

As soon as air is admitted into the muffle, oxidation commences; white fumes of lead-oxide are given off; and the bright surface of the metal becomes covered with a thin iridescent film of melted oxide, presenting brilliant spots, which move rapidly about over it. As the oxidation advances, the melted oxide is absorbed by the cupel, producing round the metal a dark patch, which gradually extends, while the metal decreases in bulk and becomes more globular. At the end of the process, when the last portion of oxide is being formed, the metal appears to be revolving rapidly, and its surface becomes very bright and iridescent; then the motion suddenly ceases, and the iridescence disappears with a kind of flash, during which the button is scarcely perceptible; after a few seconds it presents the appearance of pure silver. This last stage of the process is called the *brightening* (*éclair; Blicken*).

Owing to the fact that melted silver absorbs oxygen gas, it is necessary to remove the cupels containing the buttons of silver very gradually from the muffle, in order that they may cool slowly and not *spit* (*rocher; spratzen*), since this might occasion some loss.

When this operation has been well performed, the button of silver should separate easily from the cupel; its upper surface should be bright and smooth; the under-surface, dull and crystalline, but clean and compact. When the button is bluish above and bright underneath, without adhering at all to the cupel, it contains lead. When the upper surface of the button is flattened, dull, and wrinkled, it has either spit, or too little lead has been used and the oxidation has not been complete.

The temperature at which cupellation is conducted has a great influence on the result. Since silver is sensibly volatilisable, it is on this account essential that the temperature should not be too high. On the other hand, the heat must be sufficient to complete the oxidation of the copper and lead, and to render the oxides perfectly liquid and capable of being absorbed by the cupel. From the greater length of time occupied by the process at a low temperature, the loss of silver by volatilisation might be as great as if it took place more rapidly at an excessive heat. Experience has shown that the heat is too great when the cupels are nearly white hot and scarcely distinguishable from the metal they contain, and when the fumes appear slight and rise quickly to the crown of the muffle. In this case the oxide would be too liquid, and would carry with it into the cupels some minute particles of silver. On the contrary, the heat is too low when the fumes appear dense, creeping along the sole of the muffle, and when the oxide, being insufficiently liquid to be absorbed, collects in a ridge round the metal. In this case the loss of silver is less; but the oxidation is incomplete, and the button is likely to contain some lead. These two sources of error always obtain simultaneously, and they compensate each other more or less according to the temperature at which the operation is conducted. The best results are obtained when the cupels are only red-hot, and when the melted metal is distinctly visible and much more luminous than the cupel.

The rapidity of the current of air passing through the muffle also influences the result. Too quick a current might cause the formation of oxide more rapidly than the cupel could absorb it, or, by lowering the temperature, it might render the oxide insufficiently liquid to be absorbed by the cupel; and in either case the process would be interfered with in the same manner as if the proportion of lead to copper were too small. With too slow a current of air, the process would go on very slowly, and there would be a loss of silver in consequence of the operation lasting too long.

The most oxidisable of the various metals which may be present in an alloy are chiefly separated during the first stage of the cupellation, and towards the end, the lead-oxide formed may be almost pure, or contain only cupric oxide. Iron, tin, and zinc are oxidised with such rapidity, that alloys containing any large amount of these metals cannot be cupelled without the assay becoming chilled, or incrusted in the cupel.

The appearance of the cupels after the operation affords some indication of the kind of metal alloyed with the silver. Lead gives the cupel a pale-yellow colour; bismuth gives a slightly orange-yellow; copper gives a grey, dirty red, or brown colour, according to the quantity. Iron produces black scoriæ, which collect at the commencement of the oxidation about the edge of the cupel. Tin gives grey scoriæ, and causes incrustation when present in large amount. Zinc produces a very luminous flame, and leaves a yellowish ridge on the cupel; its presence causes loss of silver, by augmenting the volatilisation, or by spitting. Antimony gives a yellow scoria, and makes the cupel crack when present in any large amount.

When the buttons of silver have solidified, they are detached from the cupels with pliers, brushed to clean off fragments of bone-earth or oxide adhering to the underside, and then weighed. The results thus obtained give the amount of silver in the alloy too low, because there is always a loss of silver in cupellation, which in the case of ordinary alloys may amount to as much as 0·005. In the cupellation of alloys containing a large amount of silver, this loss is proportionately less than in the cupellation of alloys containing but a small amount of silver. Consequently it is necessary to apply a correction to the actual results of the assays, according to the value of the alloy in silver, as shown in the following table:—

Actual amount of Silver.	Amount found by Cupellation.	Correction for loss of Silver.	Actual amount of Silver.	Amount found by Cupellation.	Correction for loss of Silver.
1000	998·97	1·03	500	495·32	4·68
975	973·24	1·76	475	470·50	4·50
950	947·50	2·50	450	445·69	4·31
925	921·75	3·25	425	420·87	4·13
900	896·00	4·00	400	396·05	3·95
875	870·93	4·07	375	371·39	3·61
850	845·85	4·13	350	346·73	3·27
825	820·78	4·22	325	322·06	2·94
800	795·70	4·30	300	297·40	2·60
775	770·59	4·41	275	272·42	2·58
750	745·48	4·52	250	247·44	2·56
725	720·36	4·64	225	222·45	2·55
700	695·25	4·75	200	197·47	2·55
675	670·27	4·73	175	173·88	2·12
650	645·29	4·71	150	148·30	1·70
625	620·30	4·70	125	123·71	1·29
600	595·32	4·68	100	99·12	·88
575	570·32	4·68	75	74·34	·66
550	545·32	4·68	50	49·56	·44
525	520·32	4·68	25	24·78	·22

This loss of silver, however, is not constant even for the same alloys, but varies according to the mode in which the operation is conducted. For the sake of greater certainty, therefore, a *proof* assay with pure silver, or with an alloy of known value, should be made with each batch of assays, in order to ascertain whether the loss of silver be really the same as that indicated in the table for that alloy or for pure silver. The correction to be applied to the results of the assays made at the same time is then to be regulated according to the result obtained with the proof-assay. When the operation is conducted with proper care, the corrected results may indicate the amount of silver in the alloys to within 2 or 3 pts. in a thousand.

In many instances, cupellation is a very convenient method of estimating, approximately, the amount of silver in alloys and ores, but when great accuracy is required it is better to employ the wet method of assay devised by Gay-Lussac.

2. *Silver Assay by the wet process.*—This method of estimating silver consists in precipitating the metal as chloride from the solution of a known weight of the alloy, and in using for that purpose a solution of common salt containing a known amount of salt. By weighing or measuring the quantity of this solution which is just sufficient

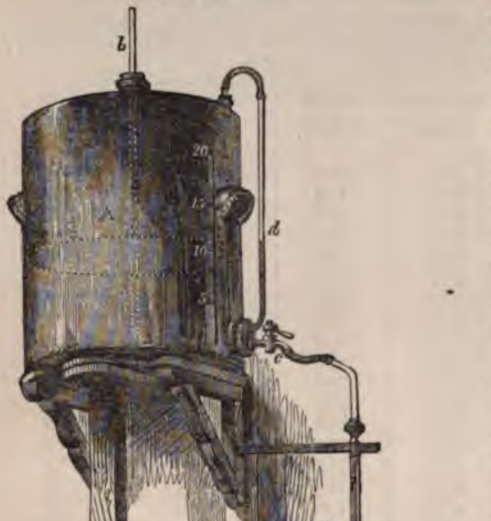
to convert the whole of the silver into chloride, it is easy to ascertain the amount of silver in the alloy. Silver-chloride separates so readily from a liquid containing nitric acid in excess, that the exact point at which all the silver is precipitated may be observed with great precision, and much more accurate results may be obtained in this way than by cupellation.

The *normal solution* is made of such a strength that 1000 grain-measures are equivalent to 10 grains of silver, or 100 cubic centimetres equivalent to 1 gramme. In many instances the normal solution may be used in the same way as any other volumetric reagent, by simply observing the volume required for perfect precipitation, and then multiplying the quantity of silver represented by 1 grain-measure or by 1 cubic centimetre by the number of grain-measures or centimetres of solution used. The amount of silver in ores and other substances may often be conveniently estimated in this way.

For the purpose of attaining a greater degree of accuracy in the results, another solution, containing only one-tenth as much salt as the normal solution, may be used for completing the precipitation. For greater convenience, in shaking the liquid to facilitate the separation of the silver-chloride, the silver-solution should be contained in a stoppered bottle.

In the valuation of alloys containing a tolerably constant and approximatively known amount of silver, such as silver coin and the bars of alloy prepared for coining, it is far preferable to take a quantity of the alloy which will contain rather more than 10 grains, or 1 gramme of silver, and to add to the solution of it in nitric acid 1000 grain-measures or 100 cubic centimetres of the normal solution at once. There will then remain only so much silver in solution as there have been in excess of 10 grains or 1 gramme. The precipitation of this portion of the silver, which should not amount to more than 2 or 3 thousandth parts, is to be effected with the decimal solution.

Fig. 746.



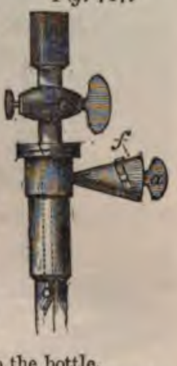
The apparatus requisite for this operation, when a large number of assays have to be made, is shown by *fig.* 746. A is the reservoir for holding a large supply of the normal solution, which can be drawn off as required by the stopcock *c*. The tube *b*, open at both ends, passes to the bottom of the reservoir, and is tightly fitted into the neck with a cork, so that there cannot be any loss by evaporation, and air can enter the reservoir only through the tube *b*.

The gauge *d* shows the quantity of solution in the reservoir.

The pipette *g*, for measuring the normal solution, has a long narrow neck and a very small aperture at the lower end, which can be closed with the finger. It is supported on a wooden frame firmly fixed to the wall, and the upper end is fitted with a collar having a conical valve (*f*) at the side. Above this collar, and forming one piece with it, is an ordinary stopcock *e*, the tube of which extends downwards through the collar into the neck of the pipette, as shown on a larger scale in *fig.* 747. To the upper side of the stopcock *e* is fitted a glass tube containing a thermometer, and communicating with the stopcock *c*.

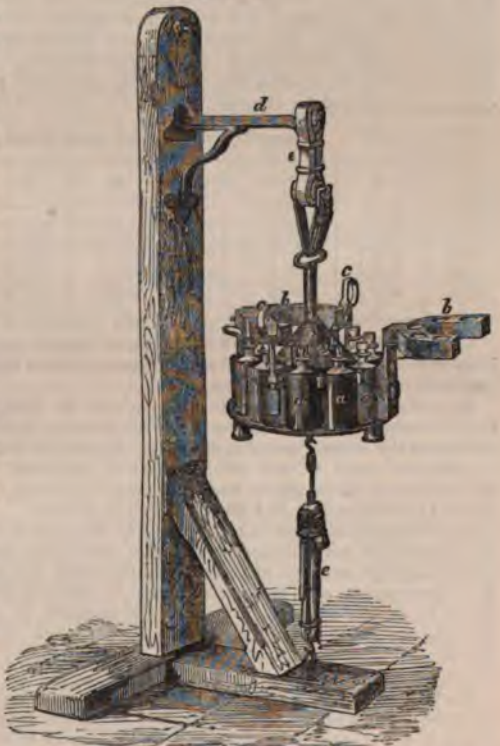
When the left forefinger is placed on the beak of the pipette, and the cocks *c* and *e* are opened, the solution cannot flow into the pipette unless the valve *f* is opened to allow the air to escape from the pipette. As soon as the pipette is filled to a little above the mark *n* on its neck, indicating the requisite volume, the cock *e* is closed; then the valve *f* is closed, and the finger removed from the beak of the pipette.

Fig. 747.



The bottle containing the solution from which silver is to be precipitated is put into the holder *h*, which is fitted to a metal plate bearing also a receptacle *i* for waste solution, and a support for a piece of sponge *k*. This metal plate slides freely between grooves from *l* to *m*, in such a way that the sponge or the mouth of the bottle containing the silver-solution may be brought exactly under the beak of the pipette. To run off from the pipette the excess of solution, the receptacle *i* is placed below the beak, and the valve *f* is cautiously opened just enough to let the level of the solution sink to the mark on the neck of the pipette. Then the valve is closed and the slide moved, so that the sponge is brought against the beak of the pipette, to wipe off the drop of solution hanging to it. As soon as that is done, the slide is moved back till the mouth of the bottle is under the beak of the pipette, and by opening the valve *f* the measured solution is allowed to fall into the bottle.

Fig. 748.



These assays are generally made in series of ten, the bottles and stoppers belonging to them being numbered and placed in a stand, which can be immersed in hot water to facilitate the solution of the alloy in nitric acid. After the metal has completely dissolved, the bottles are allowed to cool, and the nitrous vapour is displaced by blowing into the bottles through a piece of bent tube. The proper quantity of normal solution is then measured into each bottle from the pipette; the stoppers are put into the bottles; and they are transferred to an agitator (*fig.* 748), which holds ten bottles, and is suspended between two vulcanised caoutchouc springs, so that the whole of the bottles may be shaken at once.

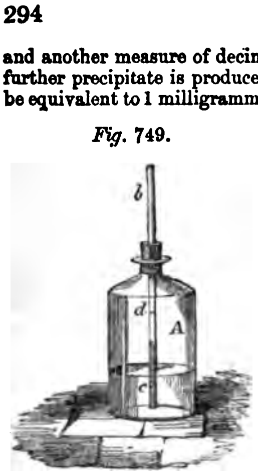
After shaking the bottles for a minute or two, they are taken out and ranged upon a black shelf, with ten compartments numbered to correspond with the bottles. When the liquid in each is clear, the stoppers are taken out and hung upon wires attached to each compartment, and a cubic centimetre of the decimal solution is run into each bottle by means of a small tubular pipette, which is fitted through a cork into the bottle, A (*fig.* 749), containing the decimal solution. In adding the decimal solution it should be allowed to flow gently down the side of the bottle, after placing the beak of the pipette, *b*, against the neck of the bottle. By this means the silver-chloride in the bottle is not disturbed, and if the liquid contains silver it is at once rendered turbid.

For each of the bottles in which a precipitate is produced by the measure of decimal solution, a mark is made on its compartment of the shelf; the bottles are again shaken, and another measure of decimal solution added—this operation being repeated until no further precipitate is produced. Supposing each cubic centimetre of decimal solution to be equivalent to 1 milligramme of silver, and 100 cubic centimetres of the normal solution to precipitate exactly 1 gramme of silver, the quantity of silver would be found by adding to 1000, the number of cubic centimetres of decimal solution requisite to complete the precipitation. If, for instance, a certain quantity of alloy (q) requires, over and above the 100 cubic centimetres of normal solution, 5 cubic centimetres of decimal solution, then the quantity (x) of silver would be 1·005 grm. The percentage (x') of silver in the alloy may then be found by a simple calculation:

$$x' : 1000 = x : q$$

And when, as in the assay of alloys that are supposed to be tolerably uniform in value, q is a constant quantity containing as a minimum 1 grm. of silver, a table may be constructed which will indicate the silver value of the alloys in thousandths, by reference to numbers corresponding with the number of cubic centimetres of decimal solution used in each instance.

Fig. 749.



The quantity (q) of alloy containing 1 grm. of silver will of course vary according to the silver value of the alloy, and the tables will relate only to particular alloys. In this country the standard of silver coin is 925 parts of silver in 1000 parts of alloy, and consequently 1·081 grm. should contain 1 grm. of silver. The quantity of alloy taken for the assay is 1·085 grm., which at the exact standard would contain 1·003625 grm. of silver, and would then require 3·5 cubic centimetres of decimal solution to complete the precipitation, and less or more according as the amount of silver in the alloy were below or above the standard. The following table expresses the value of the alloy, according to quantity of decimal solution used, within the limits of variation allowed for standard-silver:

Quantity of Alloy for Assay 1·085 *gramme.*

	0	1	2	3	4	5	6	
0	921·6	922·6	923·5	924·4	925·3	926·2	927·2	0
0·25	921·9	922·8	923·7	924·6	925·6	926·5	927·4	0·25
0·50	922·1	923·0	923·9	924·9	925·8	926·7	927·6	0·50
0·75	922·3	923·6	924·2	925·1	926·0	926·9	927·9	0·75

The numbers in the first and last columns express fractions of thousandths, which it is quite possible to estimate, after some practice, from the density of the last precipitate produced by the decimal solution.

Supposing, as in the example above given, the quantity of decimal solution used were 5 measures, then the silver value of the alloy in thousandths would be found at the top of the column under 5, or 926·2. If the fifth measure of decimal solution gave a precipitate equal to only ·0005 instead of ·001 grm. silver, then the silver value of the alloy would be rather less, and it would be found in the third line of the column under 4, corresponding to 4·50 or 925·8 thousandths.

If the amount of silver in any one of the alloys is so much below the standard that the measure of normal solution is rather more than sufficient to precipitate all the silver, the first measure of decimal solution will not of course give any precipitate. It is customary in such cases to add two or three measures of a solution of silver, which is exactly equivalent, measure for measure, to the decimal solution of salt; marking the number on the board with a *minus* sign before it, and then adding decimal salt solution. A better plan is to repeat the assay with a rather larger quantity of alloy.

Since it is difficult, by reason of evaporation and change of temperature, to ensure the constant equivalence of the measure of normal solution to the quantity of silver which it is prepared to precipitate, it is best never to attempt doing so, and accurate results may be obtained with greater certainty otherwise. For this purpose the exact value of the measure of normal solution is estimated from time to time with each set of assays by means of pure silver, of which 1·001 grm. is dissolved and treated with a measure of normal solution as a *proof* assay.

If a measure of the normal solution should happen to be exactly equivalent to 1 grm. of silver, then the first measure of decimal solution will produce a precipitate in this proof-assay, but the second measure will not produce any. If, however, a second and third measure of decimal solution be required to complete the precipitation in the proof-assay with the 1·001 grm. pure silver, then the measure of normal solution at the time will be only equivalent to 1·001 – ·003 = ·998 grm. silver, and a corresponding *minus* correction must be applied to all the other assays. Thus, for instance, in the case of one which requires 5 measures of decimal solution to complete precipitation, only 3 measures would relate to the quantity of silver over and above 1 grm. The actual quantity of silver would be 1·003 grm., and the silver value of the alloy, in thousandths, 924·4. If, on the contrary, the first measure of decimal solution gave only a very slight precipitate in the proof-assay, equal to ·00025, then the measure of normal solution would be equivalent to 1·0075 grm. of silver, and a *plus* correction of 0·75 would have to be applied to the results of the assays, before reading off the silver values of the alloys from the table, as already described.

With the exception of mercury, other metals do not interfere with the accuracy of the result obtainable by this method.

The approximate estimation of the silver value of the alloy, which is necessary in this method of assay, may be made by cupellation, or with a salt solution and burette in the usual way. B. H. P.

SILVER, BISMUTHIC. See Bismuth-Silver (i. 597).

SILVER, BLACK. }
SILVER, BRITTLE SULPHIDE OF. } See Stephanite.

SILVER, BROMIDES OF. The protobromide or argentic bromide, AgBr, occurs native as *bromargyrite*, *bromyrite*, or *bromic silver*, in the district of Plateros, and at the mine of San Onofre in Mexico; also with chloride of silver at Chañareillo in Chile, and at Huelgoet in Bretagne. It is usually found in small concretions, rarely in cubo-octahedrons. Hardness = 1—2. Specific gravity = 5·8—6. It is sectile, has a bright yellow or greenish colour, and splendent lustre. The Mexican mineral contains 57·56 per cent. silver (Berthier); the Chilian 57·43 per cent. (Field); calc. 57·45 silver and 42·55 bromine.

Argentic bromide is formed artificially by precipitating nitrate of silver with bromide of potassium. The precipitate is yellowish-white, curdy, insoluble in water and in acids, soluble in ammonia, but much less so than the chloride: according to Pohl (Wien. Akad. Ber. xli. 627), 100 pts. of aqueous ammonia, of specific gravity 0·986, dissolve 0·051 pts. of silver-bromide at 80°. It dissolves in concentrated aqueous bromide of potassium and in other alkaline bromides; also in hyposulphite of sodium, but not so readily as the chloride, and is precipitated from the solution by bromide of potassium.

Argentic bromide melts below a red heat. It is coloured greyish-violet on exposure to light, but not so strongly as the chloride. According to H. Vogel (Jahresb. 1861, p. 284), the product consists of argentous bromide, Ag^2Br. The reduction is retarded by free nitric acid, but greatly accelerated by nitrate of silver, the argentous bromide being then mixed with metallic silver, resulting from reduction of the nitrate itself. Argentic bromide is not decomposed by acids, but chlorine converts it into chloride of silver, with evolution of bromine.

The hemibromide, or argentous bromide, is produced, as above mentioned, by the action of light on argentic bromide; also by treating the corresponding oxide, Ag^4O, with hydrobromic acid. (H. Vogel.)

SILVER, CARBIDES OF. The compound Ag^4C is said by Gay-Lussac to be formed when silver is fused in a crucible in contact with lampblack. Other compounds of silver and carbon are obtained as residues in the ignition of organic silver-salts, viz. Ag^2C as a yellow residue from cuminate of silver (Gerhardt and Cahours, Ann. Ch. Phys. [3] l. 76); also as a dull white fused metallic mass, by intense ignition of silver-cyanide (Liebig and Redtenbacher, Ann. Ch. Pharm. xxxviii. 129). According to Thaulow, however (Berz. Jahresb. xxxiii. 81, 228), this last product consists of paracyanide of silver (iv. 342). The compound AgC remains as a grey powder when aqueous pyroracemate of silver is heated for some time in the water-bath. The residue left in the dry distillation of the same salt appears to be a mixture of Ag^2C and AgC (Berzelius, Pogg. Ann. xxxvi. 28). According to Regnault (Ann. Ch. Pharm. xix. 153), the monocarbide AgC is likewise obtained by heating maleate of silver.

The carbides of silver are dissolved by nitric acid, with separation of carbon, and leave metallic silver when subjected to prolonged ignition in contact with the air.

SILVER, CHLORIDES OF. Silver forms two chlorides analogous to the bromides. The protochloride or argentic chloride, AgCl, occurs native as *horn-silver* or *kerargyrite*, sometimes in cubes, octahedrons, regular dodecahedrons, and other monometric forms, but more frequently in waxy masses, sometimes columnar; no cleavage. Hardness = 1—1·5. Specific gravity = 5·31—5·43 (**Domeyko**). It has a pearl-grey, greenish, or whitish colour, turning brown on exposure, and a resinous lustre passing into adamantine. Streak shining. Translucent in various degrees. Fracture somewhat conchoidal, sectile. Klaproth found, in specimens from various localities, 73·6 to 76 per cent. silver: the formula requires 75·25 per cent. Horn-silver occurs in veins of clay-slate, accompanying other ores of silver; also with several copper ores, calcspar, heavy spar, &c. It is most abundant in Peru, Chile, and Mexico; it was formerly obtained in the Saxon mining district, but is now rare; it also occurs in Siberia, at Kongsberg in Norway, in Alsace, in Cornwall, and at Huelgoet in Bretagne. At Andreasberg, in the Hartz, an earthy variety is met with called *buttermilk ore*, which, according to Klaproth, contains 24·64 per cent. silver, 8·28 hydrochloric acid, and 67·08 alumina.

Argentic chloride is thrown down as a white precipitate, at first very bulky and curdy, when hydrochloric acid or a soluble chloride is added to any soluble salt of silver except the hyposulphite: also, together with argentic hypochlorite, by passing chlorine gas into a solution of argentic nitrate. (**Naquet**, Jahresber. 1860, p. 201.)

Precipitated argentic chloride has a specific gravity of 5·7 (**F. Mohr**, Pogg. Ann. cxiii. 655). It is wholly insoluble in *water*, so that the minutest quantity of a soluble chloride in aqueous solution may be detected by adding to it a drop of solution of silver-nitrate. The precipitate is likewise quite insoluble in *nitric acid*, even on boiling, also in dilute *hydrochloric acid*. Strong hydrochloric acid, however, dissolves it, and the solution, when left to evaporate, deposits the argentic chloride in octahedrons. The chloride dissolves easily in *ammonia*, and crystallises therefrom as the ammonia evaporates. According to **Pohl** (Wien. Akad. Ber. xli. 627), 100 pts. of aqueous ammonia of specific gravity 0·986, dissolve 1·492 pts. argentic chloride at 80°. Argentic chloride dissolves in strong solutions of *alkaline chlorides*, forming crystallisable double salts, which are decomposed by water, the silver-chloride being then precipitated. It dissolves easily also in *sodic hyposulphite*, and is not precipitated therefrom by chloride of potassium; but bromide or iodide of potassium added to the solution, throws down bromide or iodide of silver (**Field**. Zeitschr. Ch. Pharm. 1861, p. 126). The chloride is likewise converted into iodide or bromide of silver by digestion with solution of bromide or iodide of potassium, and on this reaction Field has founded a method of determining the proportions of chlorine, bromine, and iodine when they occur together in a mixture (see BROMINE, ESTIMATION OF. i. 678). *Cyanide of potassium* dissolves chloride of silver, forming chloride of potassium and argento-potassic cyanide. *Soluble sulphites* also dissolve argentic chloride.

Argentic chloride melts at about 260°, forming a transparent yellowish liquid, which, on cooling, solidifies to a horny, translucent, sectile mass. It is not decomposed by heating with charcoal, but is easily reduced by heating in a current of hydrogen, hydrochloric acid being evolved, and metallic silver separated; also by ignition with *alkaline carbonates*, an alkaline chloride being then formed, and a mixture of oxygen and carbonic anhydride evolved: *e.g.*—

$$4AgCl + 2Na^2CO^3 = 4NaCl + 2CO^2 + O^2 + 2Ag^2$$

Zinc, iron, and other easily oxidisable metals, in contact with water, quickly reduce precipitated argentic chloride to the metallic state, still more quickly if the water is acidulated with sulphuric acid. Even the fused chloride laid upon a plate of zinc or iron, and covered with acidulated water, is converted after a few days into a spongy mass of metallic silver. Weak alkaline leys do not act upon argentic chloride, but when it is boiled with a strong solution of *potash*, chloride of potassium is formed, and dense black silver-oxide is produced; the addition of *glucose* to the mixture quickly reduces the oxide to the metallic state. A similar reduction takes place when the chloride is boiled with glucose and aqueous carbonate of sodium; and this process is recommended by **Böttger** (Compt. rend. xl. 969) for obtaining pure silver from the chloride, instead of the reduction by zinc above mentioned, inasmuch as, if the zinc contains lead, which is frequently the case, that metal, being insoluble in dilute sulphuric acid, will remain mixed with the silver. **Brunner** (J. pr. Chem. xci. 254) adds chloride of silver dissolved in ammonia, by drops or in a fine stream, to a clear boiling solution of 1 pt. glucose and 3 pts. crystallised sodic carbonate in 40 pts. water, keeping up the boiling without intermission. **C. A. Müller** (Jahresber. 1864, p. 283) effects the reduction:—*a*. By boiling 6 pts. silver-chloride for half an hour with 9 pts. soda-ley, of 1·333 specific gravity, 1½ pts. clarified honey, and 8 pts. water. *b*. By digesting 6 pts. silver-chloride in the cold with 9 pts. soda-ley, 4½ pts. honey, [illegible] ammonia (specific gravity 0·925); or *c*. By digesting 5 or 6 pts.

silver-chloride at 25° for a month with 60 pts. ammonia and 9 pts. honey. (See also H. Vogel, J. pr Chem. lxxxvi. 321; Jahresb. 1862, p. 223.)

Argentic chloride quickly acquires a dark greyish-violet colour when exposed to light, the change being due to a partial or, according to some authorities, a total separation of the chlorine. The most probable view, first propounded by Wetzlar (*Gmelin's Handbook*, vi. 161), is that the reduction is only partial, resulting in the formation of a subchloride of silver. According to H. Vogel (Pogg. Ann. cxix. 497; Jahresb. 1861, p. 285), the dark-coloured compound is the hemichloride, Ag^2Cl, and is exactly similar to the product obtained by treating argentous oxide, Ag^4O, with hydrochloric acid. The reduction is retarded by strong sulphuric or nitric acid, and by ferrous salts (which absorb the chemical rays), and completely arrested by fuming sulphuric acid or mercuric chloride. In a solution of argentic nitrate, on the contrary, it takes place more quickly than in the air or under pure water, and the reduced chloride is mixed with a small quantity of metallic silver, resulting from reduction of the aqueous nitrate. Paper charged with argentic chloride is very sensitive to light, and is the material used for positive photographs, the unaltered chloride being afterwards removed by a solution of sodic hyposulphite (iii. 693; iv. 625).

Ammonio-chloride of Silver.—Dry chloride of silver slowly absorbs ammonia-gas to the amount of 17 per cent., forming the compound $3NH^3.2AgCl$, which easily gives off its ammonia when heated, and may therefore be used for the preparation of pure ammonia-gas—or of liquid ammonia, if heated in a sealed tube. Fused chloride of silver takes up only a very small quantity of ammonia (H. Rose).—A saturated solution of argentic chloride in ammonia, left to stand in a vessel not perfectly closed, deposits rhombic crystals of the ammonio-chloride, often a quarter of an inch long. A dilute solution deposits pure argentic chloride (Faraday). The ammoniacal solution is quickly reduced by zinc and copper, the silver separating as a grey mossy powder. Lead acts in the same manner, but slowly; antimony and cadmium imperfectly; iron, bismuth, and mercury, not at all. (Fischer.)

Chloride of Silver and Ammonium, or *Ammonio-argentic Chloride*, $(NH^4)Cl.AgCl$, may be obtained in crystals by placing a solution of sal-ammoniac in one arm of a U-tube, a solution of argentic nitrate in the other, the two being prevented from mixing by a plug of asbestos in the bend of the tube, and connecting them by an arc of silver plate or wire; the end dipping into the sal-ammoniac becomes covered after a while with tetrahedral crystals of the double salt (Becquerel, *Gmelin's Handbook*, i. 401). A solution of argentic chloride in boiling aqueous sal-ammoniac deposits, on cooling, nothing but argentic chloride.

Bario- and *Potassio-argentic Chlorides* are likewise obtained in tetrahedral crystals by the electrolytic method just described. (Becquerel.)

Sodio-argentic Chloride separates on cooling from a solution of argentic chloride in a hot saturated solution of common salt, in cubes, having the same form and aspect as those of common salt, but blackening when exposed to light. A more dilute salt-solution likewise dissolves chloride of silver when hot, but deposits it unchanged on cooling. The crystals of the double salt are resolved by a sufficient quantity of water into argentic chloride, and a solution of sodic chloride. (Wetzlar.)

Osmio-argentic chloride, $2AgCl.OsCl^4$, is produced on adding silver-nitrate or an ammoniacal solution of silver-chloride to a solution of sodio-osmic chloride (iv. 243), as a dingy greyish-green precipitate, which, in contact with ammonia, is converted into the minium-coloured compound $2AgCl.OsCl^4.2NH^3$. (Claus, Jahresb. 1860, p. 216; 1863, p. 299.)

Hemichloride of Silver, or **Argentous Chloride,** Ag^2Cl.—This compound is most readily formed by treating argentous oxide with hydrochloric acid, or by precipitating a soluble argentous salt (the citrate, for example) with common salt. Its formation by the action of light on argentic chloride has been already mentioned. According to Wetzlar, silver-leaf immersed in solution of ferric or cupric chloride is quickly converted into brown laminæ of argentous chloride, which must be immediately taken out of the liquid and washed with water, as otherwise they will be converted into argentic chloride. Argentous chloride is also formed on bringing silver in contact with solution of sal-ammoniac, or of cupric chloride containing that salt.

Argentous chloride heated to the temperature at which argentic chloride melts, is resolved into the latter compound and metallic silver; the same decomposition is quickly produced by the action of ammonia.

SILVER, CHLOROBROMIDE OF. The chloride and bromide of silver occur crystallised together, in various proportions, in cubes and cubo-octahedrons, also massive. The minerals thus constituted vary in hardness from 1 to 1·5; in specific gravity from about 5·75 to 6·2; and have an olive or greyish-green colour, with resinous and somewhat adamantine lustre.

Analyses.—*a. Embolite* from Chañareillo, in Chile (Field, Chem. Soc. Qu. J. x. 239).—*b.* The same (Field).—*c.* The same, from the Colorado mine, near Copiapo: regularly crystallised; specific gravity = 5·8 (Plattnex, Pogg. Ann. lxxvii. 134; lxxviii. 417).—*d.* Chañareillo (Field).—*e. Megabromite*, from Chile: crystallised in cubes and octahedrons; green; specific gravity = 6·234 (Richter, Ramm. Mineralch. p. 989).—*f. Microbromite*, from Copiapo; grey-green, becoming darker on exposure to light; specific gravity = 5·75—5·76:—

a.	*b.*	*c.*	*d.*	*e.*	*f.*
Ag^3BrCl^2	$Ag^5Br^2Cl^3$		Ag^4Br^3Cl	$Ag^9Br^4Cl^5$	Ag^4BrCl^3
16·84	19·82	20·09	33·82	26·49	12·40
14·92	13·18	13·05	5·00	9·32	17·56
68·22	66·94	66·86	61·07	64·19	70·04
99·98	99·94	100·00	99·89	100·00	100·00

SILVER, DETECTION AND ESTIMATION OF. 1. *Reactions in the dry way.*—Silver compounds mixed with *sodic carbonate*, and heated upon *charcoal* by the inner flame of the blowpipe, are reduced, yielding brilliant white metallic globules, without any incrustation of the charcoal. Heated with *borax* in the outer flame on platinum-wire, they are partly reduced and partly dissolved, yielding a white opaline glass. With *microcosmic salt* they yield in the outer flame a yellowish glass, which becomes opaline when the amount of silver is large. By daylight this glass appears yellowish, and by candlelight reddish.

2. *Reactions in Solution.*—The most characteristic reaction of saline silver-compounds in solution, is the formation of silver-chloride. Silver-salts which are insoluble in water may generally be dissolved by nitric acid, and the solution gives the same reactions as the soluble salts.

Hydrochloric acid and soluble chlorides produce a white curdy precipitate of silver-chloride, which is insoluble in boiling water and in dilute nitric acid, but is readily dissolved by ammonia. On exposure to light it gradually acquires a violet tinge, and eventually becomes black. The admixture of a small proportion of mercurous chloride prevents or retards the coloration of silver-chloride on exposure to light. In very dilute solutions of silver, the separation of the chloride precipitate takes place but slowly, and they present for some time a whitish opalescent appearance.

A precipitate of lead-chloride is distinguishable from silver-chloride by its solubility in boiling water; a precipitate of mercurous chloride is distinguishable by its insolubility in ammonia, and by turning black with that reagent.

Potassium-iodide produces a slightly yellowish-white precipitate of silver-iodide, which is soluble in excess of the reagent, very sparingly soluble in ammonia, and insoluble in dilute nitric acid.

Potassium-cyanide produces a white curdy precipitate of silver-cyanide, which is readily soluble in excess of the reagent, and insoluble in dilute acids.

Sulphydric acid and *ammonium-sulphide* produce a black precipitate of silver-sulphide, which is insoluble in ammonium-sulphide, in dilute acids, and in ammonia.

Ammonia or *potash* produces in neutral silver-solutions a brown precipitate of silver-oxide, which dissolves very readily in ammonia and in ammoniacal salts.

Alkaline carbonates produce a white precipitate of silver-carbonate, which is soluble in ammonia and carbonate of ammonium.

Sodic phosphate produces in neutral solutions a yellow precipitate of tribasic silver-phosphate, which is soluble in ammonia and nitric acid.

Oxalic acid produces in neutral solutions a white precipitate of silver-oxalate, which is soluble in ammonia, and sparingly in nitric acid.

Potassium-chromate produces a dark-brown precipitate of silver-chromate, which is slightly soluble in water, and soluble in ammonia and dilute nitric acid.

Stannous chloride in excess produces a brownish-black precipitate of metallic silver.

Ferrous sulphate produces in neutral solutions a white precipitate of metallic silver.

Zinc produces a precipitate of metallic silver; it also separates silver from silver-chloride in presence of water.

3. *Estimation and Separation.*—Silver may be separated from most other metals, and estimated with great precision as chloride. For this purpose the substance is to be dissolved either in water or nitric acid; the solution mixed with a slight excess of nitric acid, and with hydrochloric acid, as long as any precipitate or milkiness is produced, then warmed in a dark place until the precipitate has separated, and the liquid has become perfectly clear. The chloride is then collected upon a filter of known

weight, washed with acidulated water, dried, and weighed. This is the most accurate but also the most troublesome plan of weighing. The filter may be burnt, but in that case it is necessary to burn it after having separated the precipitate from it, so as to prevent as much as possible the reduction of silver. The small portion of chloride which cannot be detached from the paper is decomposed, and remains as silver in the filter-ash. The slight error which would be caused by weighing this as chloride can be rectified by warming the ash in a porcelain crucible with a few drops of nitric acid for some minutes, then adding hydrochloric acid, and evaporating to dryness. The remainder of the chloride may then be added, the whole heated till it begins to melt, and then weighed. (Compare i. 904.)

Silver may also be estimated as cyanide by adding potassium-cyanide to the solution, until the precipitate, which is at first produced, is redissolved; then adding nitric acid in slight excess, and warming. The precipitated silver-cyanide is collected on a weighed filter, dried at 100°, and weighed.

Estimation as Metallic Silver.—In the case of silver-salts from which the metal is reduced by simply heating them, this method of estimation may be conveniently adopted. The substance should be gradually heated in a porcelain crucible till the whole of the carbon is burnt.

Volumetric Estimation of Silver.—The readiness with which silver-chloride subsides in a liquid from which it is precipitated admits of the point of perfect precipitation being observed with great precision. (See SILVER ASSAY.)

The separation of silver from other metals and their salts is generally unattended with any difficulty. From solutions containing *zinc, manganese, iron, nickel, cobalt, copper, bismuth, cadmium, gold, platinum*, it may easily be separated by precipitation as chloride. From *lead* it may be separated in the same way, when the proportion of lead to silver is not large. Or both metals may be precipitated as cyanides, the silver-cyanide dissolved by an excess of the reagent, the insoluble lead-cyanide separated by filtration, and the silver-cyanide precipitated from the solution by nitric acid. Or the neutral solution may be heated with an alkaline formiate, until there is no longer any evolution of carbonic acid. Silver only is reduced, and may be collected by filtration, ignited, and weighed.

From *mercury* in the state of mercuric salts, silver may be easily separated as chloride. When silver is associated with mercurous compounds, it is best to convert them, by heating with nitric acid, into mercuric compounds, and then precipitate the silver as chloride.

From *tin, antimony, arsenic*, or *mercury*, the best method of separation is to precipitate the metals as sulphides, and heat the precipitate carefully in an atmosphere of chlorine gas, gradually raising the temperature to dull redness, so as to distil off the volatile chlorides. The silver-chloride remaining may be weighed, or the silver reduced by heating it in a current of hydrogen gas.

4. The *atomic weight of silver* has been determined in connection with those of chlorine and potassium (i. 905). Stas obtained, as the mean of a great number of experiments conducted by different processes, the number 107·943 (i. 456). B. H. P.

SILVER, FAHL-ORE. See TETRAHEDRITE.

SILVER, FLUORIDE OF. *Argentic Fluoride*, AgF. Produced by dissolving argentic oxide or carbonate in aqueous hydrofluoric acid. The solution when evaporated in a vacuum, or concentrated over the water-bath, and then left to stand, deposits large, transparent, colourless, hard prisms, mostly aggregated lengthwise, consisting of the hydrated fluoride, $AgF.2H^2O$ (Frémy, Jahresber. 1856, p. 87.—Pfaundler, *ibid.* 1862, p. 305). Marignac, on the other hand (*ibid.* 1857, p. 129), obtained the fluoride in quadratic octahedrons, containing $AgF.H^2O$. The dehydrated crystals are deliquescent, and when left over oil of vitriol, especially in a vacuum, give off water and hydrofluoric acid, and are converted on the surface into a yellow oxyfluoride (*infra*). When fused, they give off their water and leave the anhydrous fluoride AgF—not, however, quite pure, inasmuch as hydrofluoric acid and oxygen are given off at the same time (Pfaundler). When chlorine gas is passed over fused silver-fluoride, chloride of silver is formed, and fluorine is set free (ii. 673). The aqueous solution of silver-fluoride gives with hydrochloric acid a precipitate of chloride, and with potash a precipitate of oxide of silver. It is easily decomposed also by organic acids, yielding precipitates of the corresponding silver-salts, which are in this way more easily prepared than from the ordinary solution of argentic nitrate, inasmuch as they are much less soluble in free hydrofluoric than in nitric acid. (Pfaundler.)

Argentic Oxyfluoride, $Ag^4F^2O.H^2O$ or $AgF.AgHO$.—This compound is formed when a solution of the fluoride is strongly concentrated over the water-bath; also, as already observed, when the crystals of the hydrated fluoride are left to stand over oil of vitriol. It forms brass-yellow crystalline spangles, which dissolve in water with

Many other minerals—as lead, copper, iron-ores, &c.—are also regarded as silver-ores, when they contain a sufficient quantity of silver for profitable extraction (p. 279).

SILVER, OXIDES OF. Silver forms three oxides, represented by the formulæ Ag^4O, Ag^2O, and Ag^2O^2.

Hemioxide of Silver, or **Argentous Oxide,** Ag^4O. *Suboxide* or *Quadrantoxide of Silver.*—This oxide, discovered by Wöhler in 1839 (Ann. Ch. Pharm. xxx. 1), is obtained by passing hydrogen-gas over argentic oxalate, mellitate, or citrate heated to 100°, half the acid being then set free, and a dark-brown argentous salt remaining. The free acid may be removed by water, which dissolves only a small quantity of the argentous salt, but forms a brown-red or portwine-coloured solution. Argentous salts are also produced in some instances by passing hydrogen into ammoniacal solutions of argentic salts (Wöhler, Ann. Ch. Pharm. cxiv. 119). From the solid salts or their solutions, the argentous oxide is separated by caustic potash as a black precipitate. According to Geuther (*ibid.* cxiv. 121), argentous oxide is formed by the action of cuprous hydrate on solution of argentic nitrate. Wöhler (*ibid.* ci. 363) has also obtained it, mixed with metallic silver, by repeatedly boiling argentic arsenite with soda-ley.

Argentous oxide, when pure, does not change colour in drying, and does not acquire metallic lustre under the burnisher. Hydrochloric acid and hydrobromic acid convert it into argentous chloride and bromide respectively. By oxygen-acids and by ammonia it is resolved into argentic oxide and metallic silver.

According to Faraday (Ann. Ch. Phys. [2] ix. 107), a solution of argentic oxide in ammonia deposits, on exposure to the air, a body which is grey by reflected light, bright yellow in thin layers by transmitted light, and melts when heated, giving off oxygen, and leaving metallic silver.

Protoxide of Silver or **Argentic Oxide,** Ag^2O. This oxide is obtained in the pure state—

1. By heating argentic carbonate to 200°.

2. By decomposing a solution of silver-nitrate with caustic alkalis, certain precautions being, however, necessary to prevent the simultaneous formation of carbonate. *a.* The silver-solution is poured into a hot saturated solution of baryta, in such quantity as to leave the liquid with a distinct alkaline reaction; and the precipitate is left to settle in a corked flask, then drenched with cooled de-aërated water, in closed vessels. The oxide thus obtained is a brown powder, becoming black when dried at 60° or 70°.—*β.* By mixing concentrated hot solutions of potash and argentic nitrate, the oxide is at once obtained in the form of a black powder, which settles down quickly and is easy to wash.

3. By precipitating a cold solution of argentic nitrate with hydrochloric acid, washing the precipitated chloride with cold water—then levigating it with a small quantity of water, and pouring it into boiling potash-ley of specific gravity 1·25 to 1·3, so slowly as not to interrupt the boiling, the argentic chloride is decomposed, and the pure oxide is obtained as a soft bluish-black powder. If it be not completely soluble in nitric acid, it must be triturated in a porcelain mortar with fresh potash-ley and again boiled.

4. Argentic oxide is also formed when silver is very strongly heated in the oxy-hydrogen flame, or in the electric arc.

Argentic oxide is a brown or black powder of specific gravity 7·143 (Herapath), 7·250 (Boullay). According to Bineau (Compt. rend. xli. 509), it dissolves in 3,000 pts. of water, forming a solution which yields a precipitate with chlorides and phosphates, has a faint alkaline reaction, and a nauseous metallic taste. Argentic oxide is a strong base, and neutralises acids completely, forming the argentic salts. According to H. Rose (Pogg. Ann. lxxxv. 304), the recently precipitated and still moist oxide absorbs carbonic acid from the air. After drying at 60° or 70°, it is anhydrous. It gives off a certain quantity of oxygen at 100°, also when exposed to sunshine; but whether argentous oxide or metallic silver is thereby produced is not exactly known. At a stronger heat it is quickly resolved into metallic silver and oxygen.

Argentic oxide is easily reduced by oxidable substances. According to Böttger (J. pr. Chem. xc. 32), the following substances are set on fire when triturated with it in the dry state, even on paper:—sulphide of gold, black sulphide of antimony, realgar, orpiment, milk of sulphur, selenium, amorphous phosphorus, and tannic acid. Creosote also burns with scintillation when dropped on dry argentic oxide. The oxide is reduced to metallic silver completely by aqueous phosphorous acid, partially by aqueous sulphurous acid, with simultaneous formation of argentic phosphate or sulphate. Under water it is reduced to metal by contact with zinc, tin, or copper, but not by iron or mercury (Fischer). Aqueous hypochlorous acid converts it into argentic chloride, with evolution of oxygen (Balard). It is not altered by potash-ley or soda-ley, but strong aqueous ammonia converts it into fulminating silver (p. 300.)

Peroxide of Silver or **Argentic Dioxide,** Ag^2O^2.—Discovered by Ritter in 1814. It is formed when a concentrated solution of argentic nitrate is electrolysed, with two thick platinum-wires for poles, and is deposited in crystals on the positive pole, while metallic silver separates at the negative pole. The crystals, however, always contain argentic nitrate, either in combination or mechanically enclosed (Fischer, J. pr. Chem. xxxii. 108.—Gmelin and Mahla, Ann. Ch. Pharm. lxxxii. 289). According to Schönbein (J. pr. Chem. xli. 321; lxxiv. 324), pure argentic dioxide may be prepared by the action of ozone on pulverulent silver. It dissolves in cold nitric acid, to a deep brown liquid, which remains undecomposed at ordinary temperatures, deposits the dioxide when considerably diluted with water, and is resolved by heat into oxygen and argentic nitrate.

Argentic dioxide, when cautiously heated, gives off oxygen, and leaves the protoxide; but when quickly heated to 110°, it suddenly gives off oxygen with slight explosion. Hydrochloric acid converts it into argentic chloride, with evolution of chlorine. When thrown into ammonia, it rapidly eliminates nitrogen gas, and runs about in the liquid till it is dissolved. Sulphuric and nitric acid convert it into argentic salts, with evolution of oxygen. Hydrogen reduces it only when heated, but then with slight explosion. When thrown into hydric peroxide, it is quickly resolved into metallic silver and oxygen.

SILVER, OXYGEN-SALTS OF. Silver forms two classes of oxygen-salts, corresponding with the argentic and argentous oxides. The argentic salts are formed by dissolving metallic silver in oxidising acids, or by double decomposition. The nitrate, chlorate, and perchlorate are easily soluble in water; the rest are insoluble or sparingly soluble. Their reactions have already been described (p. 298.)

Argentous salts are produced by the action of reducing agents on argentic salts. Wöhler originally prepared them by gently heating argentic salts in a current of hydrogen (p. 309). In many cases, however, they are more easily obtained by passing hydrogen gas into an ammoniacal solution of an argentic salt heated to about 90°; in this manner Rautenberg (Ann. Ch. Pharm. cxiv. 119) has obtained the chromate, molybdate, and tungstate.—*Argentous chromate* is thus produced, even at ordinary temperatures, mixed, however, with a little metallic silver (to which it is completely reduced at 50°). It is a black powder, which is immediately reddened and dissolved by strong nitric acid; dilute nitric acid dissolves it with green colour, the chromic acid being reduced to chromic oxide.—*Argentous molybdate*, $Ag^4O.2MoO^3$, has been already described (iii. 1041).—*Argentous tungstate*, $Ag^4O.2WO^3$, is a black glittering powder, which under the microscope exhibits crystals apparently with rhombic faces. Nitric acid dissolves the silver from it, separating yellow tungstic acid; potash, on the other hand, extracts the tungstic acid, and separates argentous oxide. An ammoniacal solution of argentic arsenate is turned brown by hydrogen gas, and very slowly deposits a small quantity of a black powder. A solution of ferrous sulphate immediately reduces argentic arseniate and triargentic phosphate to a black powder, consisting of argentous oxide mixed with metallic silver; argentic oxalate is reduced by the same solution to metallic silver. (Jahresb. 1860, p. 200.)

A solution of *argentous citrate* or *mellitate* decomposes gradually on exposure to the air, and immediately on boiling into metallic silver and argentic salt. The same salts dissolve easily in ammonia, forming a yellowish-red liquid. Common salt added to these solutions throws down brown argentous chloride.

SILVER, PHOSPHIDE OF. When phosphorus is thrown upon melted silver, a phosphide is formed, from which part of the phosphorus separates as the fused mass solidifies, and then burns in the air. Phosphide of silver is also formed by fusing silver with glacial phosphoric acid and charcoal (Pelletier), or argentic phosphate with charcoal (Landgrebe). The phosphide obtained by the first and second methods is white, granular, and crystalline, splits under the hammer, but may be cut with a knife; it contains 20 per cent. phosphorus (AgP requires 22·3 per cent.). That prepared by Landgrebe's method is scoriaceous, brittle, sectile, exhibits a silvery lustre when filed, and contains 33·2 per cent. phosphorus (AgP^2 requires 36·4 per cent.).

When finely divided silver is gently heated in phosphorus-vapour, a blackish-grey phosphide, Ag^2P^3, is obtained, of specific gravity 4·63, easily soluble in dilute nitric acid, insoluble in hydrochloric acid: it is difficult to prepare, as if the heat applied is rather too high, some of the phosphorus is driven off. When a solution of silver-nitrate is treated with phosphoretted hydrogen-gas, a precipitate is formed, which, according to Landgrebe's somewhat doubtful statements, is a phosphide containing 15·5 per cent.

phosphorus, agreeing nearly with the formula Ag^3P^2. According to H. Rose, however, it consists of pure silver. (Handw. d. Chem. vii. 966.)

SILVER, RED, or **RUBY.** This name includes two silver-ores, both consisting of argentic sulphantimonites—viz., dark-red silver-ore, or pyrargyrite, $2Ag^2S.Sb^2S^3$, (iv. 740), and light red silver-ore or proustite, $2Ag^2S.Sb^2S^3$ (iv. 764).

SILVER, SELENIDE OF, Ag^2Se. Silver acquires a black tarnish by contact with the vapour of selenium, selenious acid, or selenhydric acid. The compound is easily formed by melting silver and selenium together. Selenhydric acid passed into a solution of silver, forms a black precipitate, which becomes dark-grey when dry, and melts without decomposition at a red heat, forming, when cold, a silver-white somewhat malleable mass. It is not completely deprived of its selenium by roasting, or even by fusion with alkalis or borax; iron unites with it, forming a dark-grey compound. Selenide of silver dissolves in boiling nitric acid, the solution containing argentic selenite. On fusing the precipitated selenide with more selenium, it is converted into the diselenide, Ag^2S^2, which melts to a specular mass, retaining its selenium on ignition, but giving it up when roasted.

Selenide of Silver and Lead.—The mineral naumannite, found at Tilkerode in the Hartz, consists of isomorphous mixtures of the selenides of lead and silver. It occurs in cubes, with perfect cubic cleavage; also massive, granular, and in thin plates; hardness $= 2·5$; specific gravity $= 8·0$; lustre metallic, splendent; colour and streak iron-black. A specimen, analysed by G. Rose, contained 23·53 per cent. Se, 65·56 Ag, and 4·91 Pb; another, analysed by Rammelsberg, gave 26·52 Se, 11·67 Ag, and 60·15 Pb ($= 98·34$). The first is nearly $PbSe.13Ag^2Se$; the second $(4—5)PbSe.Ag^2Se$.

Selenide of Silver and Copper, $AgCu'Se$ or $Ag^2Se.Cu^2Se$.—This is the composition of eukairite from Småland, Sweden (ii. 605).

SILVER, SELENIOCYANATE OF. See SELENIOCYANATES (p. 220).

SILVER, SULPHIDE OF. *Argentic Sulphide*, Ag^2S.—This, which is the only known compound of silver and sulphur, occurs native as silver-glance or argyrose, in cubes, octahedrons, rhombic dodecahedrons, and intermediate forms, occasionally also with faces of the trapezohedron and triakis-octahedron (ii. 125, 126). The crystals are often distorted and irregularly developed, or aggregated in tooth-shaped, step-shaped, dendritic, striated, filiform, or capillary groups; it also occurs in amorphous masses, and as an earthy deposit. The crystals exhibit cubic and dodecahedral cleavage. Hardness $= 2·5$. Specific gravity $= 7·196—7·365$. Lustre metallic; colour and streak blackish lead-grey; opaque; fracture small, conchoïdal, uneven. Before the blowpipe, on charcoal, it melts, swells up strongly, gives off sulphurous anhydride, and finally leaves a fused button of silver. Silver-glance occurs in veins traversing gneiss, granite, mica-slate, &c., and often in very large masses, in Saxony, Bohemia, Hungary, Norway, Siberia, Mexico, Peru, Chile, and other localities. It is seldom found quite pure, being usually more or less mixed with the sulphides of lead, copper, and iron. Pure argentic sulphide contains 87·1 per cent. silver. Klaproth found in a crystallised specimen from Freiberg 85·3, and in a massive variety from Joachimsthal 85 per cent. silver. Lindaker found in a crystallised variety from the same locality, 14·46 per cent. sulphur, 77·58 silver, 3·68 lead, 1·53 copper, and 2·02 iron ($= 99·27$).

Acanthite is a trimetric variety of argentic sulphide occurring at Joachimsthal in the Erzgebirge, in small crystals of specific gravity 7·31—7·36, isomorphous with copper-glance (ii. 76).

Argentic sulphide is formed artificially by fusing silver with excess of sulphur. According to Durocher (Compt. rend. xxxii. 823), it may be obtained in the crystalline state by mixing sulphydric acid gas with the vapour of argentic chloride. Becquerel also obtained it crystallised by filling one arm of a U-tube with solution of potassic sulphydrate, the other with argentic nitrate, and connecting the two liquids by an arc of silver. The end dipping into the alkaline sulphydrate then became covered with beautiful prisms of sulphide of silver and potassium, which were gradually decomposed by the nitric acid carried over to them, yielding sulphate of potastium and octahedral crystals of argentic sulphide. The compound is likewise formed by the action of sulphydric acid on metallic silver (p. 278), and as a brown or black precipitate when sulphydric acid gas is passed into silver-solutions.

Artificial argentic sulphide has a density of 6·85 (Karsten). After fusion, it solidifies to a lead-grey, metallic-shining, malleable mass, soft enough to be cut with a knife, and to be used for forming medallions with the die. Faraday supposed that argentic sulphide conducts electricity, like a metal, without decomposition, its conducting power however increasing with rise of temperature, like that of an electrolyte;

Hittorf, however, has shown (Pogg. Ann. lxxxiv. 1) that when free from metallic silver it conducts only in proportion as it is decomposed.

Argentic sulphide is insoluble in water, ammonia, cyanide of potassium, and dilute nitric acid; strong nitric acid however dissolves it, with separation of sulphur. It is very slowly decomposed by ignition in the air, and if the temperature is not very high, argentic sulphate is produced, which requires a very strong heat to decompose it. When ignited in hydrogen, it gives off sulphydric acid, but it is difficult to remove the whole of the sulphur even in this way. Chlorine gas does not decompose it in the cold, and acts but slowly upon it when heated (H. Rose). It is not decomposed by solution of cupric chloride, unless chloride of sodium is also present, in which case argentic chloride and cuprous sulphide are produced.

Argentic sulphide may be fused in all proportions with metallic silver. The fused sulphide is quickly decomposed by iron, with formation of ferrous sulphide and separation of metallic silver containing iron. Lead acts in like manner, the excess of lead, however, taking up the whole of the silver.

Argentic sulphide is used, in conjunction with other metallic sulphides, for producing black designs on engraved silver; this art is called *niello*. It has also been used as a hair-dye, the hair being washed first with a silver-solution (generally ammoniacal), and then with a solution of monosulphide of potassium.

Argento-cuprous Sulphide, AgCuS or $Ag^2S.Cu^2S$. *Argentiferous Copper-glance. Stromeyerite.*—A mineral intermediate in composition between argentic sulphide and copper-glance, and crystallising in trimetric forms, isomorphous with the latter; also occurring massive and embedded. Hardness = 2·5 to 3·0. Specific gravity = 6·2 to 6·3. It is sectile, has a dark steel-grey colour, shining streak, and subconchoïdal fracture. It melts before the blowpipe to a grey semi-malleable bead, gives with fluxes the reactions of copper, and when cupelled with lead, leaves a button of silver.

Analyses: *a.* From Schlangenberg in the Altai: massive (Stromeyer, Schw. J. xix. 325).—*b.* From Rudelstadt in Silesia: crystallised (Sander, Pogg. Ann. xl. 313):

	a.	*b.*		Calculated.	
Sulphur . .	15·78	15·92	S	32·0	15·73
Silver . .	52·27	52·71	Ag	108·0	53·08
Copper . .	30·48	30·95	Cu	63·4	31·19
Iron . .	0·33	0·24		203·4	100·00
	98·86	99·82			

Several massive grey silver and copper ores occurring in Chile appear, from the following analysis of Domeyko, to consist of this mineral mixed with copper-glance:

	San Pedro.		Casema.		S. Pedro.
	$Ag^2S.3Cu^2S$	$Ag^2S.4Cu^2S$	$Ag^2S.6Cu^2S$	$Ag^2S.9Cu^2S$	
Sulphur .	17·83	19·93	20·53	21·41	20·79
Silver .	28·79	24·04	16·58	12·08	2·96
Copper .	53·38	53·94	60·58	63·98	75·51
Iron .	. .	2·09	2·31	2·53	0·74
	100·00	100·00	100·00	100·00	100·00

Argentic sulphide occurs in combination with the trisulphides of arsenic and antimony, in several varieties of fahl-ore,—viz., brongniardite, freibergite, freieslebenite, polybasite, proustite, pyrargyrite, stephanite, and xanthocone. (See SILVER-ORES, p. 301.)

SILVER, SULPHOCYANATE OF. See SULPHOCYANATES.

SILVER, SULPHO-HYPOPHOSPHITE and **SULPHOPHOSPHITE OF.** See PHOSPHORUS, SULPHIDES OF (iv. 601, 602).

SILVER, TELLURIDE OF, Ag^2Te.—This compound occurs native as *Hessite* or *Telluric Silver*, in coarse-grained masses apparently monometric and granular. Hardness = 2—3·5. Specific gravity = 8·3—8·9. It is slightly malleable, has a lead-grey or steel-grey colour, and metallic lustre. Heated in an open tube, it melts but does not fume. Before the blowpipe on charcoal, it melts at a bright-red heat, leaving a somewhat brittle button of silver. With fluxes it forms in the outer flame a yellowish, in the inner flame a dark-red glass, becoming grey on cooling. It dissolves in nitric acid, the solution depositing crystallised argentic tellurite.

Analyses: *a.* From the Savodinskoi mine in the Altai (G. Rose, Pogg. Ann. xviii. 64).—*b.* Nagyag in Transylvania: specific gravity = 8·31—8·45 (Petz, *ibid.* lvii.

470).—*c.* Retzbanya in Hungary; *α.* massive; *β.* granular, with green deposit (Rammelsberg):

	a.	*b.*	*c.*		
			α		*β*
Tellurium .	36·96	36·89	37·76		33·0
Silver . .	62·42	62·32	61·55	66·28	64·5
Gold . .	. .	. .	0·69		
Iron . .	0·24	0·50			
	99·62	99·71	100·00		97·5

The formula Ag^2Te requires 37·27 per cent. tellurium and 62·73 silver.

Argento-auric Telluride, $4Ag^2Te.Au^2Te$, of specific gravity 8·72—8·83, found at Nagyag, contains, according to Petz, 34·98 per cent. tellurium, 46·76 silver, and 18·26 gold.*

Sylvanite (*q. v.*) or *Graphic Tellurium*, and *Nagyagite* or *Foliated Tellurium* (iv. 1), are likewise tellurides of gold and silver, but contain lead and antimony in addition.

SILVER, VITREOUS. Native argentic sulphide.

SILVER-ACETYL, C^2Ag^2H. (Berthelot, Bull. Soc. Chim. 1866, i. 180.)—An organic radicle, the compounds of which are obtained by the action of acetylene on ammoniacal solutions of silver salts.†

The *chloride*, C^2Ag^2HCl, is a white curdy precipitate, decomposed by boiling nitric acid, with formation of argentic chloride. Boiling hydrochloric acid decomposes it, reproducing acetylene. It does not dissolve perceptibly in ammonio-argentic chloride.

The *oxide*, $(C^2Ag^2H)^2O$.—This compound (hitherto regarded as acetylide of silver or silver-acetylene, C^2Ag^2) is produced by the action of acetylene on an ammoniacal solution of the nitrate or other oxysalt of silver, washing the precipitate with ammonia, then with distilled water, &c.

Phosphate of Silver-acetyl is a yellow curdy precipitate, decomposed by hydrochloric acid, with formation of acetylene and argentic chloride; nitric acid reproduces phosphoric acid. The sulphate is a greyish-white precipitate, exhibiting analogous reactions. An ammoniacal solution of argentic benzoate treated with acetylene yields a yellow precipitate which turns white during washing, and is found to consist entirely of oxide of silver-acetyl.

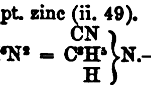
SILVER-GLANCE. Native argentic sulphide (p. 304).

SILVER-PURPLE. A dilute neutral solution of argentic nitrate mixed with stannous nitrate, or an ammoniacal solution of argentic nitrate mixed with stannous chloride, yields a brown or purple-brown precipitate, the so-called "silver-purple," the colour of which varies according to the mode of preparation. It contains tin, silver, and oxygen, and is perhaps an argentous stannate. (Handw. d. Chem. vii. 966.)

SILVER-VITRIOL. Argentic sulphate.

SIMARUBA. The bark of *Simaruba officinalis*, Dec. (*Quassia Simaruba*, L.) has long been used in medicine. It contains a bitter principle, like that of quassia-bark, and a trace of essential oil. According to Buchner, the alcoholic extract is poisonous, and acts in the same manner as the extract of quassia-bark: two grains killed a rabbit in twenty-four hours.

SIMILOR. An obsolete name for an alloy of zinc and copper containing from 6 to 9 pts. copper to 1 pt. zinc (ii. 49).

SINAMINE, $C^4H^6N^2$ = 
$\left.\begin{matrix}CN\\C^3H^5\\H\end{matrix}\right\}N$.—A basic compound discovered by Robiquet and Bussy in 1839 (Ann. Ch. Phys. [3] lxxii. 328), and further examined by Will (Ann. Ch. Pharm. lii. 1). It contains the elements of thiosinamine *minus* 1 atom of sulphydric acid, $(C^4H^8N^2S - H^2S)$, and may be regarded as ammonia, NH^3, in which 1 at. H is replaced by cyanogen, and another by allyl. It is produced in the decomposition of thiosinamine by various metallic oxides: *e.g.*—

$$\underset{\text{Thiosinamine.}}{C^4H^8N^2S} + PbO = \underset{\text{Sinamine.}}{C^4H^6N^2} + PbS + H^2O.$$

Preparation.—1. One part of thiosinamine and 5 pts. of mercuric oxide are rubbed together, without application of heat; the mass when cold is exhausted with ether; the filtrate evaporated; the viscid residue dissolved in hot water; and the solution left to crystallise (Robiquet and Bussy).—2. Pulverised thiosinamine is triturated with recently precipitated and well-washed hydrate of lead; the mixture is heated in the water-bath, till a sample diluted with water and filtered no longer produces a black colour with fresh oxide of lead and potash; the entire mass is then repeatedly boiled, first with water and then with alcohol, because the sinamine is obstinately retained by the sulphide of lead; the whole of the decoctions are evaporated to a syrup; and the crystals, which form after several months, are taken out, and freed from the syrup by gentle pressure between paper (Will). The syrup is distinguished from the crystals by its smaller amount of water; if the hydrate of lead obtained from the acetate was not well washed, the syrup contains also basic acetate of lead. (Will)

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* After deduction of 15·25 per cent. insoluble matter.

† Ammoniacal solutions of cuprous salts treated with acetylene, yield in like manner salts of cupros-acetyl, C^2Cu^2H.

Properties.—The crystals of sinamine contain $2C^4H^6N^2.H^2O$; they are white, shining triclinic prisms, which lose their lustre *in vacuo* over sulphuric acid. At 100° they melt, and give off two-thirds of their water, the melted mass forming when cold a syrup, which slowly recrystallises. By longer exposure to 100°, the whole of the water is driven off, and on cooling, anhydrous sinamine remains, as a white, opaque, slightly crystalline mass. It is inodorous, but tastes strongly and persistently bitter. It dissolves in water, alcohol, and ether. The aqueous solution has a strong alkaline reaction, and is precipitated by tannin.

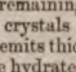
Decompositions.—1. Sinamine heated in a retort in the oil-bath, gives off ammonia from 160° to 200°, without blackening, and leaves a yellow resinous body almost insoluble in water, but dissolving sparingly in alcohol, and forming an alkaline solution. Its solution in hydrochloric acid becomes milky when mixed with ammonia, and if subsequently heated, again deposits resinous matter; the hydrochloric acid solution forms a white precipitate with mercuric chloride, and yellow with platinic chloride (Will).—2. A cold mixture of aqueous sinamine and hydrochloric acid does not give off ammonia, or become turbid on the addition of potash; but after the hydrochloric acid has been boiled, potash eliminates ammonia from it, and throws down a basic substance, which behaves like the resinous body remaining when sinamine is heated (Will). *Hydrochloric acid gas* passed over the crystals is absorbed without fusion; the resulting mass, when gently heated, suddenly emits thick white fumes of sal-ammoniac, and leaves a tumefied residue (Will).—4. The hydrated crystals, exposed to a stream of *sulphydric acid gas*, quickly assume a sulphur-yellow colour, without losing water; and if then gently heated, melt to a transparent liquid, which takes up an additional quantity of sulphydric acid, and becomes liver-coloured; but if still subjected to the action of heat, not however rising to 100°, gives off the water of crystallisation, together with sulphydrate of ammonium. Ultimately there remains a transparent, liver-coloured, inodorous mass, amounting in weight to 94·88 per cent. of the crystals. This mass forms, with water or alcohol, a solution which colours lead-salts light-red, and does not precipitate sulphide of lead till it is boiled. (Will.)

Sinamine-salts.—Sinamine expels ammonia from ammoniacal salts; it also precipitates the salts of lead, iron, and copper. Nevertheless, it does not form solid salts with any acid except oxalic acid, with which it slowly yields crystals (Will). The acid solutions impart a yellow colour to fir-wood. (Hofman, Ann. Ch. Pharm. xlvii. 55.)

Sinamine with Mercuric Chloride, $C^4H^6N^2.Hg''Cl^2$.—The solution of sinamine in aqueous hydrochloric acid forms, with excess of aqueous mercuric chloride, a precipitate which, on account of its tendency to decompose in washing, must be merely collected on a filter, strongly pressed, and dried *in vacuo* over oil of vitriol.

Platinum-compound.—Aqueous sinamine mixed with a small quantity of hydrochloric acid, forms, with platinic chloride, yellowish-white flakes, which settle down slowly, so that the filtered liquid, after standing for several hours, yields a fresh precipitate, the filtrate from that yields another, and so on. All the precipitates exhibit about the same amount of platinum (viz., about 39·6 per cent.) after drying in a current of air at 115°; hence the precipitate is perhaps $C^4H^6N^2.2HCl.Pt^{iv}Cl^4$. (Will.)

Sinamine forms a resinous precipitate with *nitrate of silver*. (Will.)



Ethylsinamine, or **Sinethylamine,** $C^6H^{10}N^2 = \left.\begin{matrix}CN\\C^3H^5\\C^2H^5\end{matrix}\right\}N$. (Hinterberger, Ann. Ch. Pharm. lxxxiii. 348.)—Produced by decomposing thiosinethylamine with hydrate of lead. When the two substances are heated together till a filtered sample no longer blackens on the addition of lead-hydrate and potash, the resulting mass boiled with water and then with alcohol, and the solutions evaporated, a dark-yellow syrupy residue is obtained, which becomes almost wholly crystalline after a few months, and when pressed between bibulous paper and recrystallised from ether, yields pure sinethylamine.

Sinethylamine crystallises in needles arranged in dendritic groups: it tastes very bitter. At 100° it melts to a colourless liquid, which when touched with a cold body, quickly solidifies in a crystalline mass, the crystallisation spreading from the point of contact. It is insoluble in water, but dissolves in alcohol and ether, forming solutions which have an alkaline reaction.

Mercury-compound, $2C^{6}H^{10}N^{2}.3Hg''Cl^{2}$.—A solution of sinethylamine forms, with aqueous mercuric chloride, a white flocculent precipitate, which, when heated over the water-bath, melts to a yellow resinous mass, solidifying in the crystalline state on cooling.

Platinum-compound, $2C^{6}H^{10}N^{2}.2HCl.Pt^{iv}Cl^{4}$.—A solution of sinethylamine in hydrochloric acid forms, with platinic chloride, reddish-yellow feathery crystals, yielding by analysis 31·55 per cent. platinum, the formula requiring 31·24 per cent.

SINAPIC ACID, $C^{11}H^{12}O^{5} = \left.\begin{matrix}(C^{11}H^{10}O^{3})''\\ H^{2}\end{matrix}\right\}O^{2}$. (Von Babo and Hirschbrunn, Ann. Ch. Pharm. lxxxiv. 19.)—An acid produced, together with sincaline, by boiling sulphocyanate of sinapine with potash or baryta-water:

$$\underset{\substack{\text{Sulphocyanate of}\\ \text{Sinapine.}}}{C^{16}H^{23}NO^{5}.CNHS} + 3KHO = \underset{\substack{\text{Sinapate of}\\ \text{Potassium.}}}{C^{11}H^{10}K^{2}O^{5}} + \underset{\text{Sincaline.}}{C^{5}H^{13}NO} + \underset{\substack{\text{Sulphocy-}\\ \text{anate of}\\ \text{Potassium.}}}{CNKS} + 2H^{2}O.$$

The best mode of preparing it is to boil the sulphocyanate of sinapine with potash-ley, supersaturate with hydrochloric acid, and purify the resulting precipitate by crystallisation from alcohol of 60 per cent. By boiling the sulphocyanate with baryta-water, the acid is obtained as an insoluble barium-salt, from which it may be separated by sulphuric acid and alcohol.

Sinapic acid crystallises in small prisms, sparingly soluble in cold, somewhat more freely in hot *water*, slightly in cold, easily in hot *alcohol*, insoluble in *ether*. It is nearly insoluble in most other acids: *nitric acid*, however, dissolves it, with red colour, apparently forming oxalic acid and a nitro-compound. *Chlorine-water* colours it, first rose-red, then purple-red, without dissolving it.

Sinapic acid melts between 150° and 200°, and solidifies from fusion in the crystalline state. When subjected to dry distillation, it turns brown, and yields a colourless oil, which, as well as the residue, forms with ammonia-gas a yellow body, slightly soluble in water.

Sinapates.—Sinapic acid forms easily soluble salts with the alkalis, sparingly soluble salts with the earths and other metallic oxides. All the sinapates, excepting the barium-salt, decompose with great facility. The solution of sinapic acid in potash- or soda-ley quickly turns red on exposure to the air, the colour afterwards changing to green and brown. The ammoniacal solution turns red-brown on exposure.

A neutral solution of potassic sinapate forms white precipitates with *chloride of calcium*, and with solution of *alum*; the latter precipitate, treated with chlorine-water, assumes first a rose-red and then a dirty-red colour. With *ferric chloride* it forms a rose-red or sometimes a purple-red precipitate, with formation of ferrous oxide. From solution of *copper-* and *lead-salts*, it throws down precipitates which soon turn blue-green; with *mercuric* and *silver-salts*, white precipitates which decompose, with separation of metal, especially on addition of more alkali.

Sinapate of Potassium is precipitated from the aqueous solution by absolute alcohol in iridescent laminæ, which soon change after the alcohol has been poured off.—The *barium-salt*, $C^{11}H^{10}Ba''O^{5}$, is prepared by precipitating the neutral ammonium-salt with chloride of barium (avoiding an excess of the latter, which would redissolve a portion of the precipitate), or by boiling sulphocyanate of sinapine with baryta-water, out of contact with air. The precipitate is to be washed with water free from carbonic acid.

SINAPINE, $C^{16}H^{23}NO^{5}$. (O. Henry and Garot, J. Pharm. xvii. 1; xx. 63.—Pelouze, Ann. Ch. Phys. [2] xliv. 214; J. Pharm. xvii. 271.—Boutron and Robiquet, J. Pharm. xvii. 279.—Fauré, *ibid.*—O. Henry and Plisson, Ann. Ch. Phys. [2] xlvi. 198.—Winckler, Repert. Pharm. xli. 169; lxvii. 257.—Simon, Pogg. Ann. xliii. 651; xliv. 593.—Boutron and Frémy, J. Pharm. xxvi. 50.—v. Babo and Hirschbrunn, Ann. Ch. Pharm. lxxxiv. 10.—Gm. xiv. 524.)—An organic base, existing as a sulphocyanate in white mustard-seed. This salt was first extracted from the fatty oil of white mustard by Henry and Garot in 1825, who at first regarded it as an acid, and called it *sulphosinapic acid*; afterwards, however, they found that the pure substance was neutral, and named it *sulphosinapisin*. Berzelius called it *sinapine*. Its true nature was first recognised by v. Babo and Hirschbrunn, who assigned to the base contained in it (the true sinapine) the formula $C^{32}H^{24}NO^{10}$, which was altered by Gerhardt to $C^{32}H^{23}NO^{10}$, or $C^{16}H^{23}NO^{5}$.

Sinapine is known only in aqueous solution and in combination with acids. The aqueous solution is obtained by gradually adding baryta-water to an aqueous solution of the acid sulphate as long as a precipitate is thereby formed: an excess of baryta must be carefully avoided, as it would immediately induce the decomposition of the base into sinapic acid and sincaline (p. 308). The aqueous solution of sinapine has a deep yellow colour, a distinct alkaline reaction, and is not precipitated either by alcohol or by ether. When evaporated it assumes a dark-brown colour, and leaves a perfectly amorphous residue. The solution forms precipitates with many metallic salts—green with cupric, yellow with mercuric, grey-brown with argentic salts: these precipitates, on standing or warming, are reduced to the metallic state. From solution of auric chloride, sinapine immediately precipitates metallic gold.

Salts of Sinapine.—These salts are colourless and more stable than the free base. Their solutions, mixed with potash or baryta-water, turn yellow, and the sinapine thereby separated is instantly resolved into sinapic acid and sincaline.

Hydrochlorate of Sinapine, obtained by decomposing the sulphate with chloride of barium, crystallises in needles very soluble in water. The solution mixed with *platinic chloride*, forms a resinous precipitate which immediately turns brown when slightly heated.

The *nitrate*, obtained also by double decomposition, crystallises in very soluble needles.

Sulphates.—The *acid sulphate*, $C^{16}H^{23}NO^5.H^2SO^4.4aq.$, is produced on adding a small quantity of strong sulphuric acid to a hot concentrated solution of the sulphocyanate in alcohol of 90 per cent., and separates on cooling in considerable quantity, so that the liquid appears completely filled with it. The crystals may be freed from adhering sulphuric and sulphocyanic acids, by washing with absolute alcohol. It forms rectangular plates, having a strong acid reaction, easily soluble in water and in boiling alcohol, nearly insoluble in ether. The crystals give off their water at 100°.—The *neutral salt*, obtained by neutralising the acid salt with baryta-water and evaporating the filtrate, is a crystalline easily soluble mass.

Sulphocyanate of Sinapine, $C^{17}H^{24}N^2SO^5 = C^{16}H^{23}NO^5.CNHS$. *Sinapine* of Berzelius; *Sulphosinapisin* of Henry and Garot.—This salt, as already observed, exists ready-formed in white mustard-seed; also, according to Henry and Garot, in the seed of black mustard and of *Turritis glabra*.

Preparation.—1. Dry mustard-powder, exhausted with ether and thereby freed from fixed oil, is treated with cold absolute alcohol as long as the alcohol acquires a reddish-yellow colour; the residue is boiled with alcohol of 90 per cent.; then pressed; and the boiling and pressing are repeated twice more. The hot-filtered tinctures yield, after half the alcohol has been distilled off, colourless crystals of sulphocyanate of sinapine, an additional quantity of which may be obtained from the mother-liquors by further evaporation and addition of sulphocyanate of potassium. Sulphocyanate of potassium likewise precipitates sulphocyanate of sinapine from the above-mentioned extracts prepared with cold alcohol.

2. Mustard-flour, freed from fixed oil by pressure in the oil-mill, is exhausted with cold and then with hot alcohol of 80 per cent.; and about half the alcohol is distilled from the united tinctures in a salt-bath, or so much, that a sample of the residue separates on cooling into two equal layers, consisting of oil and sulphocyanate of sinapine. If the concentration is carried too far, the sulphocyanate of sinapine no longer crystallises; and, on the other hand, if a sufficient quantity of the alcohol be not distilled off, part of the sinapine remains dissolved in the alcoholic oily layer, and is somewhat difficult to obtain in the form of crystallised sulphocyanate; the best way of effecting this is to add a small quantity of alcoholic sulphocyanate of potassium. The upper layer is removed; the lower watery liquid is either left to itself for a week, or as long as sulphocyanate of sinapine continues to crystallise from it; and the crystals are collected on linen, separated from the viscid mother-liquor by means of a centrifugal machine, moistened with alcohol, strongly pressed between filtering-paper, and recrystallised from alcohol of 90 per cent., then from a small quantity of boiling water, with addition of animal charcoal;—or better, the lower watery layer is mixed with alcoholic sulphocyanate of potassium, and the crystals which separate are purified as above. The mother-liquors also yield an additional quantity of sulphocyanate of sinapine on addition of sulphocyanate of potassium. (v. Babo and Hirschbrunn.)

3. Bruised white mustard-seed, freed from the greater part of the fixed oil by pressure at 50°, is exhausted with ether; the residue is digested with 7 pts. of alcohol of 80 per cent., then with 2 pts. more; the alcohol is distilled off from the tinctures till the residue is reduced to one-fourth of the weight of mustard-powder used; this residue is set aside for 14 days to crystallise; and the crystals, after being freed by ether from a red-brown matter, are purified by repeated crystallisation from water and alcohol, with addition of animal charcoal. (Winckler.)

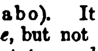
Winckler also digests white mustard with 3 pts. of alcohol of 80 per cent.; evaporates the tincture to half the weight of mustard used; treats the residue, which is covered with oil-drops, with ether, as long as the ether is thereby coloured; and purifies the residual sulphocyanate of sinapine by solution in water and recrystallisation as above. A similar process is adopted by Simon, who however, at each extraction of the mustard-flour, uses only enough alcohol to moisten it, and subjects the whole to strong pressure; by this treatment, the exhaustion is effected more quickly than when a larger quantity of alcohol is used.

Properties.—Sulphocyanate of sinapine crystallises in loose tufts of white pearly needles (Henry and Garot); in colourless, nearly transparent, glassy prisms, mostly rectangular, truncated, grouped in stars and thin nodules (Winckler). It is neutral, inodorous, tastes bitter, and afterwards hot like mustard. It melts when heated (at 130°, according to v. Babo), forming a yellow liquid, which solidifies to a gummy mass on cooling (Winckler). It dissolves with yellow colour in *water* and in *alcohol*, in greatly increased quantity when the liquid is hot, and crystallises on cooling; also in *ether*, *sulphide of carbon*, and *oil of turpentine*. (Simon.)

Decompositions.—1. Sulphocyanate of sinapine decomposes when strongly heated, giving off stinking products, and leaving charcoal (Henry and Garot); also combustible gases (Winckler). The vapours do not smell of sulphuretted hydrogen, sulphide of carbon, or hydrocyanic acid. In the course of the decomposition, volatile bases are evolved, together with gases and empyreumatic oils, which burn with luminous flame and formation of sulphurous acid (v. Babo and Hirschbrunn).—2. It dissolves readily in *oil of vitriol*, with greenish-yellow colour and slight rise of temperature, turns brown when the solution is heated, and then chars (Winckler). Sulphocyanic acid is likewise evolved (v. Babo and Hirschbrunn).—3. In contact with *iodine*, it immediately assumes a light yellow-brown colour, and when heated melts, gives off iodine, and leaves a brown-red brittle resin (Winckler).—4. Its aqueous solution is coloured by *chlorine*, first brown-red, then red, and finally yellow, with formation of sulphuric and evolution of hydrocyanic acid (Henry and Garot). According to v. Babo and Hirschbrunn, no formation of hydrocyanic acid takes place in this and similar cases.—5. With *nitric acid* of specific gravity 1·4, or less, it immediately assumes a deep red colour, giving off red vapours, and when heated turns yellow, with formation of sulphuric acid (Henry and Garot, and others).—6. When sulphocyanate of sinapine is boiled with *peroxide of manganese* and dilute sulphuric acid, the distillate contains hydrocyanic acid, and the residue contains a substance which dissolves in water, with dark brown-red colour (Winckler).—7. It dissolves with yellow colour in *caustic potash-ley*, and if the liquid be immediately supersaturated with hydrochloric acid, separates out unaltered, provided the solution is sufficiently concentrated; but when boiled with potash, soda, or baryta-water, it is resolved, as above mentioned (p. 308), into sinapic acid, sincaline, and sulphocyanic acid (v. Babo). It is likewise coloured yellow by *ammonia*, *strychnine*, *morphine*, and *quinine*, but not by *narcotine* or *salicin* (Winckler). A trace of tobacco-smoke is sufficient to produce this colouring (v. Babo and Hirschbrunn).—8. The behaviour of sulphocyanate of sinapine to *dilute acids* and saline solutions is the same as that of other sulphocyanates. *Ferric salts* are for the most part immediately reddened by it, but sometimes it is obtained in a peculiar condition, in which it does not redden ferric salts till heat is applied. (Will; v. Babo, and Hirschbrunn.)

SINAPIS. See Mustard (iii. 1067).

SINAPISINE. The name given by E. Simon (Pogg. Ann. xliii. 652; xliv. 593; l. 379), to a white, scaly, crystalline substance, which he obtained from black mustard-seed, by extraction with alcohol and ether. The examination made of it was, however, very imperfect, and the later statements contradict the earlier.

SINAPOLINE. *Diallyl-carbamide. Diallyl-urea.* $C^7H^{12}N^2O$ =  $\left.\begin{matrix}(CO)''\\(C^3H^5)^2\\H^2\end{matrix}\right\}N^2$.—
An organic base discovered by Simon (Pogg. Ann. l. 377), and further examined by Will (Ann. Ch. Pharm. lii. 25). It is formed from cyanate of allyl, by addition of water and elimination of carbonic anhydride, in the same manner as urea is formed from cyanic acid:

$$\underset{\text{Cyanic acid.}}{2CNHO} + H^2O = \underset{\text{Urea.}}{CN^2H^4O} + CO^2$$

$$\underset{\text{Cyanate of Allyl.}}{2CN(C^3H^5)O} + H^2O = \underset{\text{Diallyl urea.}}{CN^2(C^3H^5)^2H^2O} + CO^2.$$

It may be obtained very pure by boiling cyanate of allyl with water, but is more generally prepared from sulphocyanate of allyl (oil of mustard) by the action of hydrate of lead or baryta-water:

$$2CN(C^3H^5)S + 3PbH^2O^2 = CN^2(C^3H^5)^2H^2O + 2PbS + PbCO^3 + 2H^2O$$

The oil of mustard is digested in the water-bath with recently precipitated and well-washed hydrate of lead, till the latter is no longer blackened. The residue is treated with boiling water, and the solution is filtered from the insoluble sulphide and carbonate of lead: the sinapoline then crystallises on cooling.

The oil of mustard may also be boiled with baryta-water; the liquid evaporated to dryness when quite free from odour; and the sinapoline extracted from the residue by alcohol or ether. Potash or soda acts in a similar manner, but gives rise also to secondary products.

Sinapoline crystallises from aqueous solution in shining laminæ, unctuous to the touch, fusible at the temperature of boiling water, soluble in alcohol and ether. The aqueous solution is alkaline to test-paper.

Sinapoline does not dissolve in aqueous potash at ordinary temperatures, but at the boiling heat of the liquid, it melts, without giving off ammonia, to an oil which solidifies on cooling and is soluble in water.

Sinapoline does not lose weight at 100°; at a higher temperature it partly volatilises and partly decomposes.

Salts of Sinapoline.—Sinapoline dissolves easily in acids, and is separated from the solutions by ammonia. In dry hydrochloric acid gas it melts without warming; and is converted into a thick mass of the *hydrochlorate*, $C^7H^{12}N^2O.HCl$, which gives off vapours of hydrochloric acid on exposure to moist air, and is partially decomposed by water, with separation of sinapoline.

The aqueous solution of sinapoline forms precipitates with mercuric and platinic chloride.

SINCALINE, $C^5H^{15}NO$. (v. Babo and Hirschbrunn, Ann. Ch. Pharm. lxxxiv. 22.)—An alkali produced, together with sinapic acid, by boiling sulphocyanate of sinapine with potash or baryta (p. 308). To prepare it, sulphocyanate of sinapine is heated with baryta-water, till the sinapate of barium is completely separated; the filtrate, mixed with a slight excess of dilute sulphuric acid, is freed from sulphocyanic acid by precipitation with aqueous sulphate of iron or copper: the liquid is filtered from the precipitated sulphocyanate of copper; the filtrate precipitated by baryta-water; carbonic acid is passed through it; and the solution filtered from the carbonate of barium is evaporated on the water-bath: carbonate of sincaline then remains behind. By neutralising the carbonate with aqueous hydrochloric acid, digesting the hydrochlorate with oxide of silver, and evaporating the solution filtered from the chloride of silver and excess of oxide, in a vacuum or on the water-bath, sincaline is obtained as a colourless or brownish crystalline mass.

Sincaline does not volatilise without alteration; when distilled it gives off combustible vapours having an odour of methylamine, and leaves a carbonaceous residue. It has a strong alkaline reaction, and when exposed to moist air, becomes heated, deliquesces, and rapidly absorbs carbonic acid. It precipitates most metallic oxides from their solutions, even lime, baryta, and mercuric oxide. The precipitates which it forms with aluminic and chromic salts redissolve in excess of sincaline, and the chromic precipitate is reprecipitated on boiling, like a solution of chromic oxide in potash.

Sincaline dissolves *sulphur*, and on adding a mineral acid to the solution, sulphydric acid is given off, and sulphur is precipitated, which renders the liquid milky.

Salts of Sincaline.—The *carbonate*, *hydrochlorate*, and *nitrate* are extremely deliquescent. The *chloro-aurate*, $C^5H^{15}NO.HCl.AuCl^3$, is precipitated as a yellow crystalline powder slightly soluble in cold water. It dissolves easily in boiling water, and crystallises on cooling in tufts of needles. The *chloroplatinate*, $2C^5H^{13}NO.2HCl.Pt^{iv}Cl^4$, is obtained by evaporating a mixture of the hydrochlorate and platinic chloride, in splendid orange-coloured prisms or hexagonal plates.

SINESIC ACID. The name given by Lewy (Ann. Ch. Phys. [3], xiii. 446) to a fatty acid which he obtained by heating Chinese-wax with potash-lime, and to which he assigned the formula $C^{24}H^{48}O^2$.

SINETHYLAMINE. Syn. with ETHYLSINAMINE (p. 307).

SINISTRIN. This name was given by Marquart (Ann. Ch. Pharm. x. 91) to inulin prepared from dahlia-roots by boiling with water, because it turns the plane of polarisation to the left: it appears, under the microscope, to consist of opaque white spherules, disintegrates quickly in cold water, and dissolves to a colourless liquid at 75°. Inulin prepared from the roots by washing with cold water is called by Marquart synantherin: it exhibits under the microscope transparent spherules, and dissolves when boiled with water, leaving a few thin films. In other respects it resembles sinistrin.

SINNAMINE. Syn. with SINAMINE.

SINOPITE. *Bole of Sinope. Rubrica.*—A ferruginous bole occurring in masses with fine earthy fracture, in Cappadocia. It is of brick-red colour, spotted with white, dull, opaque, friable, adheres strongly to the tongue, and breaks up in water into coarse lumps, without becoming plastic like clay, or crumbling to a sandy powder like fuller's earth. It was used in ancient times as a pigment. Contains, according to Klaproth's analysis, 32 per cent. silica, 26·5 alumina, 21·0 ferric oxide, 17·0 water, and 1·5 (= 97·0) chloride of sodium. Before the blowpipe it burns hard and black.

SINTER. A name applied to incrustations, on rocks or elsewhere, from mineral waters. According to the nature of the deposit, it is distinguished as calcareous sinter (calcspar or arragonite), silicious (quartz or opal), ferruginous (pitticite), arsenical (scorodite), &c.

SIPEERINE. *Sipirine, Sepeerine.* An alkaloïd existing, together with bebirine, in the bebeeru or greenheart-tree (*Nectandra Rodiæi*), a lauraceous tree growing in Guiana. It was discovered by Rodie in 1834, and examined more particularly by Maclagan (Ann. Ch. Pharm. xlviii. 106). [For the mode of preparation see Bebirine, i. 526.]

Sipeerine forms a dark red-brown, shining, non-crystalline, resinous mass, separating from the vessel in which it is prepared in scales. It is very slightly soluble in water, easily in alcohol, either anhydrous or hydrated, but is insoluble in ether. It neutralises acids, forming olive-brown salts.

SIPOPIRA, or **SEBIPIRA.** The commercial name of the bark of *Sebipira major*, a tree growing in Brazil. The bark contains tannin, fat oil, resin, sugar, &c. (Handw. d. Chem. vii. 730.)

SISMONDIN. A mineral resembling chloritoïd, occurring in the chlorite-slate of St. Marcel in Piedmont. Melts with great difficulty before the blowpipe to a blackish glass. Analysed by Delesse (Ann. Ch. Phys. [3] ix. 388) and v. Kobell (J. pr. Chem. lviii. 40):

SiO^2.	Al^2O^3.	FeO.	MgO.	H^2O.	Undecomposed.			
24·1	43·2	23·8	—	7·6	—	=	98·7	Delesse.
25·75	37·50	21·00	6·20	7·80	0·50	=	98·75	v. Kobell.

The magnesia appears to have been overlooked in the first analysis.

SISSERSKITE. The name given by Haidinger to iridosmine from Sissersk in the Ural, having nearly the composition $IrOs^3$ or $IrOs^4$, to distinguish it from the variety found at Newjansk, the composition of which may be represented by $IrOs^8$. As, however, the two varieties crystallise in the same form, it is probable that they are not distinct mineral species, but that osmium and iridium crystallise together isomorphously in various proportions.

SISYMBRIUM. Hedge-mustard (*Sisymbrium officinale*) contains, according to Pless, allylic sulphocyanate unmixed with oxide.

SITIC ACID. The name given by Berzelius to Liebig's œnanthic acid (iv. 174).

SIXE. Gmelin's name for propylene, C^3H^6.

SKAPOLITE. Syn. with Scapolite.

SKLERETINITE. Syn. with Schleretinite (p. 204).

SKLEROCLASE, or **SCLEROCLASE.** The name applied by v. Waltershausen to diplumbic sulpharsenite, $2PbS.AsS^3$, which he regards as one of the constituents of binnite (i. 583).

SKOGBÖLITE. Nordenskiold's name for the tantalite of Skogböle in Finland, distinguished by a comparatively high specific gravity, small proportions of manganese and tin, and dark brown colour of its powder.

SKOLECITE. Syn. with Scolecite.

SKOLOPSITE. A silicate from the Kaiserstuhl in the Breisgau, occurring in lumps, with granular structure and splintery fracture. Hardness = 5·0 nearly. Specific gravity = 2·53. Colour smoke-grey, greyish, or reddish-white. Translucent on the edges. Slightly brittle. Before the blowpipe it fuses like vesuvian, with intumescence and spluttering, to a shining greenish-white glass enclosing small bubbles. With borax it slowly forms a colourless bead; with phosphorus-salt the same, and a skeleton of silica; with soda it yields the reaction of sulphur. In the pulverulent state it is easily decomposed by hydrochloric acid, with separation of gelatinous silica. It contains, according to the mean of v. Kobell's analyses (J. pr. Chem. xlvi. 484), [illegible] silica, 17·9 alumina, 2·5 ferric and ferrous oxides, 8·9 manganous oxide, 15·5 lime, 2·2 magnesia, 11·5 soda, 1·3 potash, 4·1 sulphuric anhydride, and 0·9 chloride of sodium, which may be approximately represented by the formula

$Na^2SO^4 . 6(M^2 ; \bar{M}'')SiO^3 . \overset{\prime\prime\prime}{\bar{Al}}{}^4Si^3O^{12}$.

SKORIAN. Breithaupt's name for a variety of spinel, closely allied to hercinite, and containing, according to John, 63·0 per cent. alumina, 23·0 ferrous oxide, 6·0 magnesia, 6·0 silica, together with magnesia and other constituents not determined. It occurs at Bischofsheim in the Rhöngebirge, and at Hinter-Hermsdorf, near Schandau in Saxony. (Handw. vii. 999.)

SKORILITE. A scoriaceous mineral from Juan del Rio del Calvaxio in Mexico, containing, according to R. Thomson (J. pr. Chem. viii. 506), 58·0 per cent. silica, 16·8 alumina, 13·3 ferrous oxide, 8·6 lime, and 2·0 water. It occurs in brown masses, containing numerous cavities. Streak white. Hardness = 2·0. Specific gravity = 1·70. Before the blowpipe it becomes lighter in colour, but does not melt. With fluxes it gives the iron reaction.

SKORODITE. Syn. with SCORODITE.

SKORZA, or **SCORZA.** A variety of EPIDOTE (ii. 489).

SKOTIN. Syn with Bucklandite, or lime and iron epidote.

SKUTTERUDITE. An arsenide of cobalt, $CoAs^3$, occurring at Skutterud, near Modum, in Norway (i. 1042).

SLIBOWITZ. *Slibowitza, Slivowitz.* An ardent spirit, prepared in Bohemia and Hungary, by distilling the fermented juice of plums.

SLOANITE. A mineral from the gabbro of Tuscany, occurring in radiated masses, cleaving distinctly parallel to the faces of an orthorhombic prism of 105°. It is white, opaque, with pearly lustre. Hardness = 4·5. Specific gravity = 2·441. Melts before the blowpipe, with intumescence, to a white enamel. Dissolves in acids, with separation of gelatinous silica. Contains, according to Bechi (Sill. Am. J. xiv. 64), 42·2 per cent. silica, 35·0 alumina, 8·1 lime, 2·7 magnesia, 0·3 soda and potash, and 12·5 water: probably a decomposed zeolite.

SMALT. A beautiful blue glass, prepared (chiefly in Saxony) by melting roasted cobalt-ore with silica and potash. The ore (arsenide or sulpharsenide containing nickel, copper, and iron) is first roasted to such a degree as to oxidise the cobalt and leave the nickel, iron, and copper in combination with arsenic and sulphur. Four or five parts of this roasted ore are then mixed with 10 pts. of ground calcined quartz and 4 pts. of potassic carbonate, and the mixture is slowly melted in pots arranged on a furnace resembling that used in glass-houses. The oxide of cobalt then unites with the fused potassic silicate, forming a deep blue glass, while the mixed arsenides and sulphides of nickel, copper, and iron fuse and collect at the bottom of the pot, in the form of a brittle metallic-looking mass called speiss, which is used for the preparation of nickel. The pot is then skimmed, and the glass is ladled out and poured into cold water, by which it is split into innumerable fragments. The broken glass is stamped to powder and ground under water between granite stones, in a vessel through which a gentle stream of water is constantly flowing. The water carrying the powdered smalt in suspension is made to pass through a number of depositing vessels, so arranged that the overflow of each shall pass into the next. Moreover, each of these vessels is larger than the one which precedes it, so that the time during which the washings are retained in them goes on progressively increasing, and the deposited particles continually increase in the minuteness of their subdivision, the colour becoming less intense the greater the degree of subdivision of the particles. (*Miller's Elements of Chemistry*, 3rd edit. ii. 555. For further details, see *Ure's Dictionary of Arts*, &c. i. 784, and *Handw. d. Chem.* vii. 1000.)

Smalt is essentially a potassio-cobaltous silicate, sometimes approaching nearly to the formula $(K^2O.Co''O).6SiO^2$. Its composition is, however, subject to considerable variation, as the following analyses by Ludwig (J. pr. Chem. li. 129) will show:—

	Norwegian: deep-coloured.	German: deep-coloured.	German: pale; coarse.
Silica	70·86	66·20	72·12
Potash and Soda	21·41	16·31	20·04
Cobaltous oxide	6·49	6·75	1·95
Alumina	0·43	8·64	1·80
Ferrous oxide	0·24	1·36	1·40
Arsenic Anhydride	trace	. .	0·08
Water and Carbonic Anhydride	0·57	0·92	0·46
	100·00	110·18	97·85

SMALTINE. Native cobaltous arsenide, $Co''As^2$ (i. 1041).

SMARAGDITE. A granular actinolite of emerald-green or grass-green colour, sometimes occurring intergrown with augite of similar colour. Mixed with garnet it forms the rock called eclogite, and occurs also in gabbro mixed with saussurite or labradorite.

SMARAGDOCHALCITE. Syn. with ATACAMITE (i. 429).

SMECTITE. A term sometimes used as a synonym of *fuller's earth*; applied also more particularly to an argillaceous mineral from Cilly in Lower Styria, analysed by Jordan, and another from Condé in France, analysed by Salvétat. (See SILICATES OF ALUMINIUM, p. 259.)

SMELITE. An aluminic silicate from Telkebanya in Hungary. (See SILICATES, *loc. cit.*)

SMILACHIN. The name given by Reinsch (Repert. Pharm. lxxxii. 145) to a crystalline substance which he obtained from the root of *Smilax China* (L.).

SMILACIN. Syn. with SARSAPARILLIN (p. 198).

SMITHSONITE. Syn. with Calamine, or native carbonate of zinc (i. 713).

SOAP. *Savon. Seife.*—In ordinary language, the term soap is applied only to the potassium- and sodium-salts of the fat-acids—stearic, palmitic, oleic acid, &c.,—produced by the action of potash and soda upon the fats; but in scientific language, the same term is extended to all the metallic salts of the fat-acids, among which the lime-soap obtained as a secondary product in the stearic acid manufacture, and the pharmaceutical preparation called lead-soap or lead-plaster, obtained by heating olive-oil with oxide of lead, may be particularised as being of practical importance.

The ordinary neutral fats—such as tallow, palm-oil, olive-oil, cocoanut-oil, &c.—are the glyceryl-salts or glyceric ethers of the fat-acids (see GLYCERIDES, ii. 881); and their conversion into soaps, or saponification, by the action of alkalis or other bases, is the converse of the process of etherification, consisting in the separation of the glyceryl and the acid-radicle, and an interchange between the glyceryl and the metal of the alkali, resulting in the formation of an alkaline salt of the fat-acid—that is to say, a soap—and glycerin: thus with stearin (neutral glycerylic stearate) and potash:

$$\begin{array}{ccccccc}
\left.\begin{matrix}(C^{18}H^{35}O)^3\\(C^3H^5)'''\end{matrix}\right\}O^3 & + & \left.\begin{matrix}K^3\\H^3\end{matrix}\right\}O^3 & = & \left.\begin{matrix}(C^3H^5)'''\\H^3\end{matrix}\right\}O^3 & + & \left.\begin{matrix}(C^{18}H^{35}O)^3\\K^3\end{matrix}\right\}O^3.\\
\text{Stearin.} & & \text{Potassic hydrate (3 at.).} & & \text{Glycerin.} & & \text{Potassic stearate (3 at.).}
\end{array}$$

The ordinary method of saponifying neutral fats consists in boiling them with solution of caustic potash or soda. Most fats require long-continued boiling with excess of alkali to convert them completely into neutral soaps; some, however (as lard, beef-marrow, and oil of sweet almonds), may be saponified by agitation with caustic alkali at ordinary temperatures. Alkaline carbonates also decompose the neutral fats when boiled with them; but the process, when conducted under the ordinary atmospheric pressure, is very tedious, and does not yield a perfect soap. Complete saponification may, however, be effected by boiling neutral fats with solutions of alkaline carbonates under increased pressure, as in the apparatus patented by Tilghman (ii. 886), in which a mixture of the neutral fat and alkaline solution is forced by a pump through a long coil of iron tubing heated to 350°—400° F.

The fat-acids (stearic, oleic acid, &c.), when already separated from glycerin, are easily saponified by the action of alkaline carbonates; in this manner soap is extensively prepared from the crude oleic acid or red oil (iv. 192), obtained as a bye-product in the manufacture of stearic acid. Resins also, which are chiefly mixtures of acid compounds, easily decompose alkaline carbonates and form soaps.

As the neutral fats occurring in the vegetable or animal body are not simple glycerides, but mixtures of several compounds of that class (stearin, palmitin, olein, &c.) it follows that the soaps resulting from their saponification will be mixtures of the potassium- or sodium-salts of two or more of the corresponding fat-acids, the soap being, *cæteris paribus*, more solid in proportion as the acids of higher melting-point and atomic weight predominate in it.

The properties of soap depend also in great measure on the alkaline base contained in it. Potash-soaps are deliquescent, and do not dry up when exposed in solution to the air, but retain so much water as to form a soft slimy jelly: when artificially dried they absorb a large quantity of moisture, and likewise become converted into a jelly. This kind of soap is called soft soap, in contradistinction to the soda-soap, or hard soap. The latter neither retains so much water, nor does it absorb so much as to render it soft; but hardens when exposed to the air, and with a certain amount of water forms a perfectly solid mass, in which it is difficult to make impressions with the finger.

100	parts of dry potassic	oleate	absorb from the air	162	parts of water.
100	,, ,, ,,	palmitate	,, ,,	35	,, ,,
100	,, ,, ,,	stearate	,, ,,	10	,, ,,
100	,, ,, sodic	stearate	,, ,,	7½	,, .

Soft soap is made from train-oil and the drying vegetable oils, such as linseed oil, hard soap from tallow, and the non-drying vegetable fats and oils, and mixtures of these with rosin. Rosin by itself forms a soft soap, either with potash or with soda.

Every kind of soap found in commerce contains a variable quantity of water, partly in chemical combination. Hard soap becomes harder by drying, so that at last it can be pulverised. Potash-soap decomposes the salts of sodium, *e.g.* common salt, or sulphate of sodium, forming chloride or sulphate of potassium, and a soda-soap. It is, indeed, in this indirect manner that hard (soda) soap is sometimes manufactured in Germany.

Soap is perfectly soluble in alcohol and in hot water. The aqueous solution is more thickly fluid and slimy than the alcoholic solution, but both solidify to a jelly at a certain stage of concentration; opodeldoc is soap mixed with alcohol in this state of concentration. Potash-soap is more readily soluble in water than soda-soap. This is better seen with the salts of the pure fatty acids than with ordinary soap. Stearate of sodium undergoes hardly any change when brought together with 10 parts of water, whilst stearate of potassium is converted by it into a thick jelly. Oleate of sodium is soluble in 10 parts of water, oleate of potassium in 4 parts, and forms a jelly even with 2 parts of water; palmitate of potassium is converted by 10 parts of water into a stiff transparent jelly.

Cold water does not dissolve the alkaline oleates, palmitates, and stearates, which constitute ordinary soap, without decomposition, the neutral salts being thereby resolved into alkali which dissolves, and into an acid salt which is precipitated. The same decomposition occurs when hot solutions of soap (particularly weak solutions) are cooled.

This reaction explains why, in using soap, even with the purest water, a whitish turbidity (*soapsuds*) is always obtained; the alkaline property of soapsuds is due solely to the liberation of a portion of caustic potash or soda, which removes the fatty impurities in water.

Soap is quite insoluble in a solution of *common salt* containing more than 1 part of salt in 400 of water: hence, on adding a certain quantity of salt to the contents of the soap-pan, consisting of soap already formed mixed with glycerin and excess of alkali, and continuing the boiling for a certain time, the soap ultimately separates completely from the watery liquid, and rises to the surface, in the form of a granular mass or curd, while the glycerin and alkaline salts remain dissolved at the bottom of the pan, constituting what are called "spent leys," and may be drawn off or pumped out. The soap may then be ladled out or run off into iron or wooden frames, and left to cool and solidify.

All varieties of soap are not separated with the same ease from their solutions, by means of salt. Thus soap made from cocoanut-oil requires a much larger quantity of salt to separate it from solution than soap made from tallow, the former being soluble in saline solutions, in which the latter is perfectly insoluble. Rosin-soap is affected by common salt in the same manner as the soaps from fat.

The same results as those obtained by the use of common salt are also produced, although in a less energetic manner, by chloride of potassium (which acts but slightly), alkaline carbonates, sulphate of sodium (also very weak in its action), acetate of potassium, and sal-ammoniac. In weak caustic ley, soap is perfectly soluble: in strong ley, on the contrary, or when the concentration of the ley is increased by boiling, the soap separates in the same manner as from a solution of common salt. For this reason, soap-boilers are in the habit of using weak ley, particularly in the beginning of their operations, as stronger ley, in separating the soap, would prevent the necessary amount of contact amongst the ingredients, and very much retard the process of saponification.

It is impossible, during the preparation of soap, entirely to avoid the presence of earths and metallic oxides. These, consequently, decompose a small portion of the soap, combining with the fatty acid, which they take from the alkali. Portions of lime and magnesia constantly accompany the caustic ley, and are brought with it into the boiling-pan, and the sides of the vessel are always sufficiently acted upon to impart a visible trace of iron or copper to the soap. The soaps formed with lime, magnesia, iron, and copper are not soluble, and they are much less rapidly softened by heat than the corresponding alkaline compounds. They are disseminated, however, in such a minute state of division throughout the mass of hot soap, as almost amounts to solution. As the soaps of iron and copper possess the colours peculiar to the salts of those metals, the whole mass of soap acquires by their presence a uniform greenish or blue colour, partly caused by the sulphur contained in the ley (particularly in soda-ley), forming sulphide of iron or copper. When a soap of this kind is allowed to cool rapidly, the cut surface presents a uniformly coloured appearance, something like wet slate. If the mass, however, cools slowly, the soaps of the earths and metallic oxides separate from the great bulk, and collect into larger or smaller groups in different parts with a certain degree of regularity, giving a *marbled* or *mottled* appearance to the cut surface. The substances which impart the mottled appearance to soap, are only held in suspension in consequence of its thick state of fluidity. The mottled appearance may therefore be entirely removed, and white soap produced, by adding a certain quantity of water, so that those substances may subside, while the soap is still in a perfectly liquid state in the boiling-pan. This additional quantity of water is not again separated, but remains with the soap. Great importance was formerly attached in commerce to the mottled appearance of the soap, as affording a sure indication that the amount of water in the soap cannot exceed a certain limit. Methods have, however, been discovered of imparting any kind of mottled appearance to soap containing much more water than the ordinary curd-soap, by mixing mineral colours with it when it has attained a certain stage of hardening. The dark-coloured mass formed by the subsidence of the impurities above mentioned is technilly called "niger" or "nigre," and is sometimes used for mottling other soaps.

Hard Soaps.—These soaps, as already observed, are made with non-drying oils, or solid fats, and soda. Their hardness is in proportion to the amount of stearic and palmitic acid which they contain. Soda-soaps, made with drying oils, such as linseed-oil, are pasty, and easily liquefied by a small quantity of water; in fact, they approach to the character of soft soaps made with potash.

The most important kinds of hard soap are those made with tallow and with olive-oil, the former material being used in England and other northern countries, the latter in the South of Europe.

The following description, by Mr. Gossage, of the English method of making hard soap, is taken from Richardson and Watts' *Chemical Technology* (i. [3] 679):—

"The fatty and oily materials which are used for the production of hard soaps in this country are tallow, palm-oil, and cocoanut-oil, also rosin, the whole of which are saponified by soda.

"The manufacturer provides himself with solutions of caustic soda of various strengths, called 'leys,' these being obtained by boiling together a solution of carbonate of soda and slaked lime, running off the first solutions, and washing the residual carbonate of lime with several affusions of water—the last liquors thus obtained being used for dissolving a fresh batch of carbonate of soda.

"It is a well-known fact that lime, in whatever proportion it may be used, does not effect the perfect decomposition of carbonate of soda, unless the latter is present as a weak solution. And as any alkali in the state of carbonate which may be introduced into the soap-copper is incapable of decomposing the neutral oils or fats, it becomes wasted; therefore the manufacturer uses solutions of carbonate of soda of such strength as will yield leys (solutions of caustic soda) having a specific gravity not exceeding 1·090.

"Soap-pans are made of various sizes, some being as large as 15 feet diameter and 15 feet deep, capable of yielding 25 to 30 tons of finished soap in one operation. They are at the present time constructed of wrought-iron plates joined together by rivets. The contents of these pans are usually caused to boil by the injection of free steam through a number of small holes in a circular bent pipe, which is in connection with a steam-boiler. The pans are also sometimes heated by means of fires placed underneath the lower part, or by steam-chambers formed round the lower part of the pans.

"The manufacturer charges his soap-pan at the commencement with a quantity of neutral oil or fat, and adds to this weak leys having a specific gravity of about 1·050°. He causes steam to be injected to produce ebullition and mixing. If the process goes on properly, the oil or fat which was previously floating on the surface of the ley becomes speedily combined therewith, producing a uniform milky emulsion, from which no watery particles separate on cooling. If this combination does not take place, the operator adds either water or weaker ley, and continues the boiling until the perfect emulsion is produced; at this period all taste of alkali in the compound has passed away—the tongue being used, in place of turmeric-paper, to ascertain the presence of free alkali. The combination of the oil or fat with the mineral alkali, or the displacement of the glycerin, having been thus fairly put in progress, the operator makes repeated additions of stronger leys, continuing the boiling until he finds the presence of free alkali in the compound; he then adds more oil or fat, or some rosin; he also continues to make repeated additions of stronger leys. In this part of the operation he takes care that there shall be no excess of alkali present in the compound at the period when the soap-pan has become nearly filled by the repeated addition of oils or fats and leys. He then adds common salt to the mixture, which, by its superior affinity for water, as compared with that of the saponaceous compound, effects the decomposition of the emulsion, and causes this to be separated into soap combined with a definite quantity of water, but not having its full proportion of alkali, and a solution of common salt, which latter contains the glycerin of the fats or oils employed. The soap floats in a granulated state on the surface of the solution, which is then called 'spent leys,' and should contain no free alkali. After a few hours for subsidence, the exhausted solution or spent ley is withdrawn from the soap-pan from under the imperfectly made soap, and is rejected as worthless.

"The workman commences his second operation by the addition of some weak ley to the imperfect soap, and by boiling he brings the contents of his pan again into a state of homogeneous mixture,—called the 'close state' as contradistinguished from the condition in which the soap is granulated and separated from the liquid contents of the pan; and if he has not already added his full complement of oils or fats, he completes the addition of these, adding also strong leys, until he finds the mixture has acquired a strongly alkaline taste. He then adds sufficient common salt to cause the separation of the soap from the alkaline solution, and boils the soap for some hours in the presence of the alkaline solution, to ensure the whole of the fatty matter being combined with alkali. If it is intended that the product should be framed as a 'curd' soap, it is allowed to remain quiescent for a few hours, so that the leys may subside; and the soap is then skimmed off and transferred to the 'frames,' in which it solidifies by cooling, and is then divided, by cutting with wires, into slabs and bars ready to be delivered to consumers. If the soap contains rosin as part of its acid constituents, it requires a further operation before framing. This consists in melting the curd-soap (after abstraction of the alkaline leys from the lower part of the pan) with the addition of water, and boiling the mixture by steam or fire, or both steam and fire, so as again to produce a homogeneous compound, containing an indefinite proportion of water, and allowing this compound to remain quiescent for two days, when a separation takes place, resulting in the elimination of a definite compound, containing about 65 p.c. of fatty acids, 6·5 of soda, and 28·5 of water. This forms the upper stratum of the contents of the soap-pan, underneath which is an indefinite compound, technically called 'nigre,' containing a much larger proportion of water. When it is judged that the separation of these compounds has been well effected by subsidence, the upper portion, or the definite compound, is usually taken out of the soap-pan by ladling, and transferred to frames, to solidify by cooling. The residual portion, which contains an excess of alkali as well as of water, is boiled up with salt and the addition of fatty materials, to form part of the succeeding boil of soap.

"The nigre, removed as above described, is particularly well adapted for making mottled soap. For this purpose it is treated with the usual finishing ley for a mottled soap, and boiled till it is fit to be transvased into the frames. The quantity of nigre obtained from one fitting or purifying operation is not enough to be conveniently boiled by itself; it should therefore be saved, and six or more batches operated upon at a time. Occasionally a portion of bone-fat may be added, and the soap finished as ordinary mottled soap."

The method of making olive-oil soap, as practised in France and Italy, and the modern German method of making tallow-soap, are similar in principle to the above. The old German method consisted in saponifying the tallow with potash, and converting the resulting potash-soap into a soda-soap by decomposition with common salt. This method, brought to great perfection by long experience, enabled the manufacturer to prepare an excellent soap from very impure materials; but the increasing price of potash, and the cheapening of soda, have caused it to be nearly abandoned for the modern method of saponification by soda alone. For details of these methods, and for figures and descriptions of the machinery used in soap-making, see *Chemical Technology*, vol. i. pt. 3.

Cocoanut-oil Soap; Marine Soap.—Cocoanut-oil differs in constitution from other vegetable oils and from tallow, and its reaction with saponifying agents is also quite peculiar. The soap prepared from it can only be separated from solution by very strong solutions of common salt; in fact, it is soluble in dilute brine, and is therefore serviceable for washing in saltwater: hence the name *Marine Soap.*

Cocoanut-oil soap is prepared with the strongest soda-ley, of specific gravity 1·16 (20° Bm.), and by using perfectly pure and caustic ley, and avoiding excess as much as possible, the process of salting out may be dispensed with. The saponification is facilitated by the addition of potash to the soda.

Pure cocoanut-oil soap hardens much too quickly to exhibit any distinct formation of curd, and is consequently incapable of marbling by itself: it is very white, translucent like alabaster, exceedingly light, and forms a good lather, but always possesses a disagreeable savour. No means have as yet been made known to remove this smell, although it appears that several manufacturers are possessed of the secret. An important property of cocoanut-oil soap is its power of combining with more water than can ever be communicated to tallow-soap, and this property of the soap frequently gives rise to dishonest traffic. Cocoanut-oil actually produces no greater quantity of soap than an equal weight of tallow, but the soap from the former can easily be made to absorb one-third more water or ley. Ordinary soap treated in the same manner, or containing the same quantity of water, would be so soft that it would yield easily to the pressure of the thumb; but cocoanut-oil soap neither exhibits any want of consistence or softness, nor does its appearance in any way indicate the fraudulent practice which has been adopted in its manufacture.

A remarkable fact observed by soap-boilers, but by no means satisfactorily explained, is that cocoanut-oil is saponified with so much the more difficulty the more rancid it has become.

In general, cocoanut-oil is not saponified alone, but is employed as an addition to tallow, &c., for the purpose of producing quickly-solidifying soaps containing a large proportion of water, which could not be obtained from tallow alone. It is even possible to prepare soap on a large scale in a few hours, without salt, and almost without fire, by the use of cocoanut-oil and tallow, which are merely warmed together with strong ley sufficiently to melt the fat, and kept in a constant state of agitation.

The different kinds of cocoanut-oil soap, which all belong to the class of soaps containing a considerable quantity of water, are marbled artificially. Marbling or mottling of this kind is not dependent upon the production of *Curd* and *Flux*, but is simply a mechanical effect, carried out in the following manner:—The blue or red colour (bole, &c.) is rubbed up with a residue of the soap, or better with a separate portion of good cocoanut-oil soap, until the whole acquires a uniform red or blue colour. This is now scooped into the form in alternate layers with the colourless soap, and by stirring the mass together, streaks and veins are produced in all directions.

Castor-oil Soap.—Castor-oil is readily saponified by strong soda-ley. The product is white, amorphous, and translucent, and possesses considerable hardness, even when it contains as much as 70 per cent. of water. (Soeber, Dingl. polyt. J. cxxxviii. 306.)

Palm-oil Soap.—This soap is boiled with caustic soda, nearly in the same manner as tallow-soap. It has an agreeable but powerful smell, and a yellow colour when the oil is used in an unbleached state, but is white, with a very slight odour, when the oil has been bleached. Palm-oil is seldom used as soap-stock without the addition of some other fat: 3 lbs. of palm-oil to 1 lb. of tallow forms a good soap. An inferior article, called "demi-palme," is obtained from 1 lb. of palm-oil with 4 lbs. of tallow.

Palm-soap, when carefully prepared from pure materials, possesses emollient properties, which, combined with an agreeable odour, render it well adapted for toilet purposes. In France a good toilet-soap is prepared from a mixture of 9 parts of palm-oil and 1 part of cocoanut-oil; and a demi-palme soap, also for the toilet, with 11 parts of white tallow, 3 parts of palm-oil, 1 part of cocoanut-oil, and 1 part of purified yellow resin.

Rosin (or Yellow) Soap.—Colophony at the boiling temperature, when it is perfectly fluid, combines with the alkalis much more rapidly and with greater ease than the fats themselves. The soap separates on the surface, when an excess of carbonate is used, or in presence of common salt, as a thick slimy brown mass, smelling strongly of rosin, and containing 15·8 per cent. of dry soda. The amount of water in this soap, although not exceeding 27 to 30 per cent., is nevertheless sufficient to communicate to the soap a smeary viscid consistence, which is not altered by long exposure to the air. The attraction of the soap for water is so great, that it becomes liquid on exposure, after having been previously dried artificially.

Although rosin-soap by itself is thus unfitted for use, an excellent and perfectly firm product is obtained by its combination in certain proportions with tallow and palm-oil soap. The amount of rosin in this mixture should not exceed one-third of the fat; 15 per cent. of rosin makes a good soap, but beyond that limit, the soap is depreciated in colour and firmness. The grease-stock of which this kind of soap is generally made consists of kitchen-fat, bone-fat, and red oil.

The best plan of preparing this soap, is to saponify the rosin and tallow separately, and to mix the two soaps in the boiler, where they are retained in a state of ebullition for some time, until a uniform mixture has been effected; salt is then added, and the soap brought into the moulds. It is not advisable to mix the separate soaps in the moulds, which is a plan sometimes adopted. In this country and in America, where rosin-soap was first manufactured, it is usual to add the rosin, in the form of coarse powder, with the last quantity of ley, to the fatty (palm-oil or tallow) soap, consequently before the boiling is finished; and to boil the mixture with the necessary addition of ley for completing the formation of the resinous compound. This point is attained when a cooled specimen presents the proper consistence, and leaves no film of rosin when used for washing the hands. The boiling finishes with the addition of some weak ley to the soap, which has already separated from the under-ley; this addition is made in order to facilitate the deposition of the impurities with which commercial colophony is always mixed; the soap is then carefully filled into the moulds.

Rosin-soap thus prepared has a brownish colour, which passes into that of yellow wax when palm-oil is used, and this of course requires no previous bleaching. It is very firm, somewhat rough to the touch, and very translucent. The best quality exhibits on the cut surface a fibrous structure like that of wood. It produces an excellent lather, but always retains the smell of rosin. The low price of rosin renders this soap cheap, and for common washing purposes, where the smell is not an objection, it is a highly useful product.

Red Oil or Oleic Soap.—This oily acid is much used for the manufacture of soap, the saponification being easily effected, inasmuch as the acid is already separated from the glycerin, and has merely to enter into combination with the alkali.

It may be prepared by boiling 1300 lbs. of soda-ley of 18° B. in the kettle, and treating it in separate portions during stirring with 1000 lbs. of red oil or oleic acid.

Oleic acid is also frequently used, together with tallow or beef-marrow—for instance, 3 pts. of oleic acid to 2 pts. of the neutral fat—also with rosin.

Campbell Morfitt has patented a process (1858, No. 588) for preparing soap with red oil or other fat-acid and carbonate of soda, in the form of *barilla, kelp, trona, sal-soda, soda-ash, bicarbonate of soda*, &c.

The red oil, or other fatty acid, is poured into an open pan with a fire beneath, or, preferably, into a kettle or tub, which it fills to one-third of the depth, and agitated and heated by steam twirl. If it is desired to make a grade of soap lower than toilet-soap, rosin is to be added in small lumps as soon as the oil has become hot. The proportion of rosin may range from 5 per cent. of the fat-acid used and upwards. When, after continued heating and stirring, the rosin becomes entirely dissolved, carbonated alkali, finely powdered, is to be added portionwise to the homogeneous mixture of fat and rosin, while the twirl is kept slowly revolving. When all the alkali is in, and the intumescence has subsided, the paste will begin to thicken, and will promptly assume the condition of soap. At this stage it is shovelled out into the frames, and left to settle.

For neutral soaps, the quantity of carbonated alkali should only slightly exceed the chemical equivalent proportion, and must be determined by calculation from the combining number of the fat-acid which constitutes the "stock." For strong soaps, the quantity may be increased several per cent. beyond that proportion. For toilet-soaps the rosin is omitted.

The relative proportions of fat, rosin, alkali, and water in this soap being adjusted at the beginning, there is no waste ley or any other residue; and the soap is said to come out promptly, and in greater perfection than can be readily obtained by the usual method of boiling soap upon caustic ley. The soap is always uniform in appearance and composition, and does not shrink or deteriorate by time and atmospheric influence. It wastes slowly in water, gives a rich lather, and whitens the clothes.

Soft Soap.—The substance commonly called "soft soap" is a more or less impure solution of potash soap in caustic ley, forming, at ordinary temperatures, a transparent smeary jelly. If an attempt were made to separate this soap from the ley by means of salt, the potash-soap would be converted into hard soda-soap by the chloride of sodium.

The materials employed in this country for making soft soap are whale-oil, seal-oil, linseed-oil, and tallow; on the Continent, hemp, linseed, camelina-oil, and poppy-oil (which belong to the class of drying oils, and do not become solid at 0° C.) are used; also the different varieties of rapeseed- and train-oils, which do not dry up, and become partially solid at 0° C. The former produce a softer kind of soap, the latter soap of firmer consistence; it is therefore usual to mix the oils in different proportions, according to the season of the year, choosing the drying oils in the winter, and the others for the summer, when the market-price admits of this selection being made.

In boiling soft soap, the weaker leys from 9° to 11° B. (specific gravity 1·06 to 1·08) are first used, and a moderate heat is applied, and kept up until complete combination is effected,—*i.e.*, until a thick sticky fluid falls in streaks from the stirrers; this ought to possess a shining appearance, and although it may be somewhat turbid, should not resemble soap separated by means of salt.

As soon as these characters clearly appear, the clarification is commenced by the gradual addition of stronger ley. This is kept up at intervals until the mass of soap assumes the appearance of a transparent slime, a drop of which let fall on a glass plate remains clear on cooling without exhibiting any fatty border, which would indicate incomplete saponification: if, on the other hand, there is an excess of ley, the drop is granular without lustre, and a grey skin gradually spreads over its whole surface. When the right proportions have been attained, the excess of water is removed by evaporation, the fire being increased and the evaporation accelerated by beating the froth with stirrers, so as to renew the air over its surface. As evaporation proceeds, the soap becomes thicker, its colour becomes darker, and less froth is produced. At last the froth is so much diminished that the soap sinks, and the bubbles are so far larger that they resemble films or lamellæ, which overlap and cover each other upon the surface. This is what the soapboilers term the *lamination*, and the noise occasioned by the process gives rise to the saying, "The soap talks." The soap is now really finished, but another specimen or test is taken before it is scooped out into the moulds. When this no longer shows any opaque zone, after having cooled for some time, or only in a very slight degree, it may be safely concluded that the proportions in the pan have been properly attained. The fire is then extinguished, the soap is left for some time longer in the pan to cool, and packed in small casks for sale.

There are two kinds of soft soap known in commerce, the composition of which is as follows:—

	First quality.	Second quality.
Fat-acids	50·0	40·0
Potash	11·5	9·5
Water, &c.	38·5	50·5
	100·0	100·0

Some kinds of oil, hempseed-oil for example, impart to the soap a green colour, which is much prized by consumers: hence it is often artificially produced, by mixing the soap with indigo precipitated by potash from its solution in sulphuric acid.

A so-called corn or grain is sometimes produced in soft soap by the addition of tallow. The soap then retains its ordinary character, but fine granular particles of a crystalline structure are observed in it, consisting probably of salts of stearic and palmitic acids. The formation of this grain requires a certain degree of heat, and can only be effected in the colder seasons of the year, at temperatures between 9° and 15° C. (48° and 59° F.). This process is called "figging;" it is practised merely from habit, and no useful object is gained by it. Attempts have been made to imitate this useless appearance in a manner calculated to injure the quality of the soap. Thus, for instance, slaked lime has been used, with the production of a lime-soap, and even starch has sometimes been mixed up with the soap.

All kinds of soft soap exhibit a strong alkaline reaction, and are characterised by a penetrating disagreeable odour, which, however, does not necessarily resemble that of the fats employed. The smell is most perceptible in soaps prepared from train-oil, and is due to the presence of potassic valerate.

Soft soap is used to some extent for washing coarse linen, but it is of far greater importance, as an indispensable and powerful detergent, in the linen-bleaching works.

Soda Soft Soaps.—According to Gentele's recent experiments on a large scale, the potash-base of soft soaps may in part be replaced by soda, without disadvantage to the resulting soap. The product has the characteristics of soft soap, but contains a little more water. The leys must be free from salt and other saline impurities, as they prevent the clarifying of the soap. The best proportion is 1 pt. of soda to 4 pts. of potash-ley. A mixture of 100 lbs. of red oil, 50 lbs. of tallow, and 3,750 lbs. of hempseed-oil makes a good stock for this soap.

All the soft soap (*savon vert*) made in Belgium and Germany contains about equal proportions of soda- and potash-soaps.

A soft soap of firm consistence (*white soft soap*) may also be made by melting together 75 pts. of tallow or tallow-oil, and 25 pts. of cocoanut-oil, and boiling the mixture with ley till the paste sharply bites the tongue. At this stage, salt solution of 20° B. is added, to give consistence to the paste, and the soap on cooling is then ready to be barrelled.

Toilet Soaps.—These soaps consist either of very pure ordinary curd-soap, or of soaps prepared by the cold process (p. 314) with lard, beef-marrow, or sweet-almond oil, and perfumed in either case with various essential oils. To refine an ordinary soap—which should, of course, be as free as possible from colour and impurity—for toilet purposes, it is reduced to shavings, and melted over a water-bath with rose and orange-flower water and salt, 24 lbs. soap being thus mixed with 4 pints of rosewater, 4 pints of orange-flower water, and two large handfuls of salt. The next day, if entirely cooled, the soap is cut up into small bars and dried in a shady place, then melted anew in the same quantities of rose and orange-flower water, and strained; afterwards cooled and dried again. This done, the soap will be free from bad odour. It must be powdered, and exposed for several days to the air, but protected from dust. It is then ready to receive the intended perfume, and to be moulded and pressed into the desired forms.

Another method is to melt 6 lbs. of best white soap in 3 pints of water, and when liquid to strain it through a linen cloth. It is then placed in a kettle with a pint of water and a tablespoonful of salt; a brisk fire is kindled under it; and the contents are whipped or stirred to make them foam and froth. The fire is then put out; the balling continued till the mass is sufficiently inflated; the fire again kindled; and the kettle kept on till its contents swell and foam. It is then emptied into the cooling frames, and after solidification taken out, cut into cakes, and pressed.

The perfumes used are chiefly volatile oils—viz., the oils of roses, bergamot, mallow, lavender, thyme, rosemary, lemon, verbena, vanilla, bitter-almond; nitrobenzene is also used instead of the last mentioned oil.

Toilet-soaps are coloured blue with ultamarine, red with vermillion, brown with an alkaline solution of burnt sugar. A peach-blossom tint is said to be produced by adding a little cream of tartar to soap which has been perfumed with bitter-almond oil.

Toilet Soft Soap, or *Shaving Cream*, is made by gradually beating 50 lbs. of lard with 75 lbs. of caustic potash-ley marking 17° Bm.

Glycerin Soap, which is used as a toilet-soap for softening the skin, is made by mixing glycerin with ordinary soap when transferred to the frames.

Light or *Flotant Soap*.—This soap is prepared by threshing or agitating a solution of soap, to which one-fifth or one-sixth part of water has been added, with a rouser or paddlewheel, until the lather has risen to twice the height of the soap-solution, and then transferring it to the moulds. A soap is thus obtained inflated with air, which gives it sufficient buoyancy to float on water.

Transparent Soap is prepared by drying ordinary soap in a stove, dissolving it in hot alcohol, leaving the solution at rest to allow the impurities to settle down, or removing them by filtration, the filter being supported on a funnel surrounded with hot water, then distilling off the alcohol till the residue acquires such a consistence as to solidify when cooled in metallic moulds.

Silicated Soaps.—Silicate of sodium (soluble glass) is a compound possessing considerable detergent power; in fact, the alkali contained in it is held in a state of feeble combination, similar to that in which it exists in soap made with fat. When mixed with ordinary soap, it forms a mixed soap of greatly reduced price, and very useful as a cleansing agent for domestic use, and in many manufacturing processes. Some of the so-called silicated soaps, however, are mere mechanical mixtures of silicious substances (such as fine sand, alumina, fuller's-earth, &c.) with ordinary soap: these are comparatively worthless.

The value of the true silicated soaps was recognised at the Great International Exhibition of 1862, by the award of a prize-medal to W. Gossage & Sons, for "Excellent Samples of Silicated Soaps." The manufacture of these soaps is now carried out on a most extensive scale.

For hard soaps, the soluble glass is prepared by melting together, in a reverberatory furnace, 9 pts. of soda-ash (containing 50 per cent. of caustic soda) with 11 pts. of clean sand; and for soft soaps, equal weights of carbonate of potash and sand. To effect solution, the glass, after being drawn off into moulds and quenched with water, is either ground in a mill and then boiled with alkaline water; or it is placed in lumps in an iron vessel having a false bottom, and water is poured into the vessel in sufficient quantity. The mixture of the soluble glass and soap is effected by a mechanical stirring apparatus worked by steam-power.

When it is desired to produce a compound soap having less detergent power than the compound soaps obtained by mixing genuine soaps of ordinary quality with solutions of soluble glass, a portion of the alkali contained in the solution may be neutralised by combining it with rosin or with fatty or oily acids. The combination is effected by boiling the rosin or the fatty or oily acids with solution of soluble glass, in the same manner as rosin and other soap-making materials are combined with alkali in the ordinary process of soap-making.

Gossage also reduces the quantity of free alkali in his silicated soap by neutralising it with sulphuric, hydrochloric, sulphurous, or carbonic acid, added either before or after the incorporation of the glass with the soap. The carbonic and sulphurous acids are passed into the liquid in the gaseous form.

Mixed Soaps of various kinds. Numerous processes have been devised and patented for reducing the cost of soap by mixing it with various substances—*e.g.* gelatin ground bones, dextrin, oleaginous seeds, potatoes, glue, wool, cotton, &c., some of which are said by the inventors to increase the detergent power of the soap; also for the so-called saponification of various kinds of animal refuse (such as stale fish, intestines, skins, hoofs, &c.) by boiling them with alkali; but most of the soaps thus prepared are worthless articles, or if they have any value at all, it is simply in proportion to the amount of genuine soap made from fat contained in them.

The late Dr. Normandy patented several processes for the preparation of "salinated soap." This soap contains the sulphates and carbonates of sodium and potassium, or sulphate and hydrosulphite of sodium, added while the soap is yet in paste. One process consists in adding to 80 lbs. of soap, 28 lbs. of sulphate of sodium, and 4 lbs. of carbonate of potassium, or 2 lbs. of carbonate of potassium and 2 lbs. of carbonate of sodium. Or, if the substanees are used singly, then to 80 lbs. of soap add only 32 lbs. of sulphate of sodium, 15 lbs. of carbonate of potassium, or 10 lbs. of carbonate of sodium. As this soap contains an excess of alkali, it may perhaps answer well for marine use.

The addition of these salts renders the soap harder, and, according to the inventor, renders it possible to prepare a useful soap from several cheap oils, which would otherwise yield a soap too soft for ordinary use. Sulphite and hyposulphite of sodium have also the property of removing the chlorine which bleached fabrics are apt to retain, and by which they are deteriorated.

(For further details respecting these mixed soaps, and various other patent soaps, see *Chemical Technology*, i. [3], 716.)

Railway and Waggon Grease.—The grease or soap used for diminishing friction on the axles of carriages is of two kinds. The one, called "locomotive grease," adapted for high velocities, is prepared by heating palm-oil, or a mixture of palm-oil and tallow, with a solution of sodic carbonate, whereby an imperfect soap is produced. The grease thus prepared is used for passenger-carriages, and lately also for such goods and mineral waggons as are provided with axle-boxes.

The other kind, called "antifriction" or "waggon-grease," is adapted for low speed, and is used for waggons having no axle-boxes. It was originally prepared by agitating rosin-oil (obtained by distillation of colophony) with milk of lime in a pulpy condition; but the present high price of rosin has compelled manufacturers to employ several cheaper substitutes for it—such as paraffin residues mixed with coal-tar, residues from candle-making, cotton-seed oil, fish-oil or footes, pitch-oil, the heavier parts of American petroleum, &c. (*Chemical Technology*, i. [3], 742; [5], 555.)

Analysis and Valuation of Soap.

The value of soap depends mainly on the amount of dry soap (the dry compound of alkali with the fatty acid) contained in it, and this is easily ascertained by exposing a weighed specimen, in the form of thin shavings, to the heat of a drying stove or over oil of vitriol till its weight no longer diminishes. The residue is dry soap, and the loss of weight is hygroscopic water, or water which has been purposely added to the soap, either in the pan after it has been brought to the state of curd, or after its transference to the frames.

To determine the proportion of fat-acid and alkali, the dried soap is decomposed by a measured volume of standard sulphuric acid, and the fat-acids and rosin which rise to the surface are collected on a weighed filter, washed with hot water, dried in a vacuum, and weighed. The weight expresses the joint amount of fatty and rosin-acids in the soap. Cold alcohol will dissolve out the fatty acid, together with a small quantity of rosin, and the filter dried in a vacuum, and weighed again, gives approximately the amount of rosin.

The nature of the fat-acids may be determined by their consistency and melting-point. If oleic acid greatly predominates, so that the fat-acids show but little tendency to solidify, the quantitative estimation may be facilitated by the addition of a weighed quantity of white wax.

The quantity of sulphuric acid neutralised by the alkali in the soap is determined by means of the quantity of a standard solution of caustic soda required to neutralise the excess of acid remaining after the decomposition (see ALKALIMETRY, i. 117, 261). This determines the quantity of alkali in the soap; and the total amount of water, alkali, and fatty acids deducted from the weight of soap analysed, gives the quantity of foreign matter present, which, if the soap is unadulterated, should not exceed 1 per cent.

The amount of alkali in soap may also be determined by incinerating the soap in a muffle. The residue then consists of sodic or potassic carbonate, which may be weighed, and the quantity of alkali thence calculated if the soap is genuine, or determined by the alkalimetric method if other substances are likewise present.

Cailletet (Bull. Soc. ind. de Mulhouse, xxix. 8) has proposed a method of analysis by which only one weighing is required—viz., that of the quantity of soap analysed. The soap (10 grammes), in thin shavings, is decomposed by a measured volume of sulphuric acid of known strength in presence of a measured volume of oil of turpentine. The fatty acids thus liberated dissolve in the oil of turpentine and increase its volume, and this increase, multiplied by the specific gravity of the fat-acid, determines its weight. The amount of alkali is then determined in the manner just described, and the water is estimated by difference: this, of course, implies that the soap is genuine, otherwise the difference will include the foreign matter as well as the water.

The standard acid is prepared by mixing 189·84 grammes of the strongest sulphuric acid, H^2SO^4, with sufficient distilled water to make up the volume to a litre at 15° C. Of this acid, 10 cubic centimetres neutralise 1·2 grammes of soda (Na^2O), and are therefore sufficient to decompose 10 grammes of soap, the amount of alkali in which never exceeds 12 per cent.

10 cubic centimetres of the standard acid and 20 cubic centimetres of oil of turpentine are poured into a tube containing 50 cubic centimetres, and divided into 100 equal parts. 10 grammes of the soap in thin shavings are then added, the tube is closed with a good cork, well shaken for a few minutes till the soap is dissolved, and then left at rest for a quarter of an hour, till the oily solution of the fat-acids has completely separated from the watery liquid.

The volume of this oily solution is now to be read off, a deduction of half a division, or $\frac{1}{4}$ cubic centimetre, being made to allow for the diminution of the capacity of the tube, and consequent rise of the level of the oil, occasioned by the thin film of watery liquid which adheres to the inner surface of the tube.

In an experiment made with olive-oil soap, the total volume of liquid in the tube after agitation and standing was 79·5 divisions, and that of the watery liquid 26 divisions: hence the volume of the oily solution was $79·5 - 26·5 = 53$ divisions, or 26·5 cubic centimetres. Deducting from this the volume of turpentine-oil added, the remainder ($= 6·5$ cubic centimetres), is the volume of the fat-acids in the soap.

To determine the specific gravity of these fat-acids, 10 grammes of the same soap were dissolved and decomposed by sulphuric acid; 10 grammes of white wax were then added. The union of this wax with the separated fatty acids was promoted by heating, the whole then left to cool, and the cake of wax separated from the liquid, dried between filtering-paper, and weighed. Its weight was 15·97 grammes, which diminished by 10 grammes, the weight of the wax added, gives 5·97 grammes as that of the fat-acids in the soap; and this divided by 6·5 cubic centimetres, the volume of the fat-acids obtained from the same quantity of soap, gives 0·918 for the specific gravity of these fatty acids. By similar experiments with different kinds of soap, the specific gravities of the fat-acids contained in them were found to be, on the average:

	Specific Gravity of Fat-Acids.
Olive-oil (Marseilles) soap	0·9188
Cocoanut-oil soap	0·940
Palm-oil soap	0·922
Tallow soap	0·9714
Soap from oleic acid	0·9003

When rosin-soap is shaken up with dilute sulphuric acid and oil of turpentine, scarcely any of the rosin is dissolved. If fat-acids are likewise present, these dissolve in the oil of turpentine; but the quantity of rosin dissolved is only sufficient to increase the volume of the turpentine-oil (20 cubic centimetres), by $\frac{15}{100}$ cubic centimetre. The undissolved rosin collects below the turpentine as a bulky layer, so that in this way the presence of rosin in a soap can easily be detected.

Bolley's Method.—One gramme of the soap is decomposed in a small beaker-glass with ether and acetic acid. Two layers of liquid are then quickly formed, the upper being an ethereal solution of the fat-acid (or rosin), and the lower an aqueous solution of alkaline acetate and of the salts contained in the soap, whilst insoluble admixtures are left in various forms, according to their particular nature. The two liquids are separated by a pipette; the ethereal solution is evaporated in a tared glass over the water-bath, and the residual fat-acid (or rosin) is weighed.

The watery liquid is evaporated to dryness in a platinum-dish, the residue is ignited, and the amount of alkali (remaining as chloride and sulphate) determined by the usual method.

Gräger's Method.—The soap, cut in thin shavings, is dissolved in alcohol of 30 per cent., the quantity of solvent used being such that 100 grammes of soap shall yield a litre of solution. All impurities are then left behind, together with a certain quantity of sodic or potassic carbonate; 10 cubic centimetres of the solution, clarified by standing, are then diluted with water, and precipitated by chloride of calcium. The precipitate, consisting of the calcium-salts of the fat-acids, is washed, dried at 100° C., and weighed. 100 parts of this precipitate correspond, according to Gräger, with 100·5 parts of anhydrous soap, that is of sodic stearate, the result not being perceptibly affected by the fact that the acid of soap is not pure stearic acid, but likewise contains palmitic and oleic acids.

The extreme limit of water in genuine hard soap is 20 per cent. for mottled, 25 for white, and 30 for yellow soap. The proportion of alkaline bases is mostly from 8 to 9 per cent., and that of the fat-acids from 60 to 70 per cent. In yellow soap, part of the fat is replaced by 10 to 20 per cent. of rosin, and soaps made from cocoanut-oil contain a much larger amount of normal water than those made from tallow or olive-oil. But the above proportions may be regarded as standards of comparison; and any deviation from them indicates a deterioration in the quality of the soap, either from excess of water, or from the substitution of some foreign substances for the normal constituent of the soap. (See further *Chemical Technology*, i. [3], 729; [5], 318.)

SOAPSTONE. *Soap-rock. Pierre de Savon. Seifenstein. Steatite* in part.—A soft massive mineral, occurring in veins in serpentine at the Lizard Point in Cornwall and elsewhere. It is brittle after drying, has a greasy lustre, and white, yellowish, bluish, or reddish colour; does not adhere to the tongue. Specific gravity = 2·20. Before the blowpipe it gives off water and blackens; thin splinters fuse with difficulty on the edges. Perfectly soluble in sulphuric acid.

Analyses.—*a.* From Lizard Point (Klaproth, *Beiträge*, ii. 180; v. 22).—*b.* From the same (Svanberg, Pogg. Ann. liv. 267; lvii. 165).—*c.* Gae Grease, Cornwall (Haughton, Phil. Mag. [3], x. 253).—*d.* Kynance Bay, Cornwall (Haughton).—*e* Frankenstein in Silesia: *Kerolite* (Maak, Schw. J. lv. 304).—*f.* Svärdsjö in Dalarne, Sweden: *Piotin* or *Saponite* (Svanberg, *loc. cit.*).—*g*, *h.* North shore of Lake Superior: *Thalite* (Smith and Brush, *loc. cit.*):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Silica . .	45·00	46·8	42·10	42·47	37·95	50·89	48·89	45·60
Alumina . .	9·25	8·0	7·67	6·65	12·18	9·40	7·23	4·87
Ferric oxide .	1·00	0·4	. .	. .	. .	2·06	2·46	2·09
Magnesia . .	24·75	33·3	30·57	28·83	18·02	26·52	24·17	24·10
Lime . .	. .	0·7	. .	. .	. .	0·78	. .	1·07
Potash . .	0·75	. .	. .	. .	. .	. .	0·81	0·45
Soda . .	. .	. .	. .	. .	. .	. .		
Water . .	18·00	11·0	18·46	19·37	31·00	10·50	15·66	20·66
	98·75	100·2	98·80	97·32	99·15	100·15	99·22	98·84

These analyses cannot be reduced to any single formula: indeed, it is doubtful whether any of the minerals to which they refer are definite compounds.

SOAPWORT. *Saponaria officinalis.*—The root of this plant, which contains saponin (p. 192), is used for washing and cleansing dresses, &c. (See *Ure's Dictionary of Arts*, iii. 719.)

SODA. This term, in scientific language, is applied to the anhydrous protoxide of sodium, Na^2O, or the hydrate, NaHO, but in technological language, it denotes also the neutral carbonate, Na^2CO^3 or $Na^2O.CO^2$. The mode of occurrence of this salt in nature and its properties have been described under CARBONATES (i. 702). It was formerly prepared from the ashes of marine plants, chiefly from certain species of salsola, some of which (viz., *Salsola clavifolia* and *S. Soda*) yield an ash containing more than 40 per cent. of neutral sodic carbonate. But the quantity obtained from these sources at the present day is altogether insignificant compared with that which is produced from common salt by the mode of decomposition invented by Lablanc, and consisting:

1. *In converting chloride of sodium into sulphate by heating it with sulphuric acid.*
2. *In converting the sulphate into carbonate by heating it with chalk or limestone and coal.*

A brief outline of this process is given under CARBONATES (i. 702), and a full account of it, with figures and descriptions of the apparatus used, will be found in Richardson and Watts's *Chemical Technology*, (i. [3], 204—295; [5], 234—265). In the present article we shall enter somewhat more fully into the theory of the second part of the process, the "balling process" as it is called, especially with reference to recent investigations.

Dumas suggested, for the explanation of Leblanc's process, a theory which may be expressed by the equation:

$$2Na^2SO^4 + 3CaCO^3 + C^9 = 2Na^2CO^3 + CaO.2CaS + 10CO.$$

T [illegible] which was for many years universally received as correct, supposes that the black ash or ball-soda contains an oxysulphide of calcium, $CaO.2CaS$. This compound has never been isolated, but its existence was assumed, because it was believed that if the calcium in the ball-soda existed as oxide and sulphide not combined together in the form of an insoluble oxysulphide, the carbonate of sodium and sulphide of calcium would, when brought in contact with water, immediately decompose one another, forming sulphide of sodium and carbonate of calcium. A similar theory of the process was given by Unger (Ann. Ch. Pharm. lxxxi. 328), who assigned to the supposed oxysulphide the composition $CaO.3CaS$. Kynaston (Chem. Soc. Qu. J. xi. 155) supposed the ball-soda to contain an insoluble compound of sulphide and carbonate of calcium, $CaCO^3.2CaS$.

Gossage however pointed out, in the specification of a patent obtained in 1838 (No. 7416), that the undissolved residue remaining from the lixiviation of black ash with water, consists almost entirely of monosulphide and carbonate of calcium, not chemically combined, but merely mixed; further, that this monosulphide of calcium is perfectly insoluble in water, and therefore does not decompose the sodic carbonate when the black ash is treated with water, such decomposition taking place only in so far as a portion of the monosulphide may have been converted into a soluble polysulphide during the treatment in the furnace.

These results are fully confirmed by the recent experiments of Dubrunfaut (Bull. Soc. Chim. 1864, i. 240), Scheurer-Kestner (*ibid.* 169), Pelonze (Compt. rend. [1866], liii. 314), and especially of J. Kolb (Ann. Ch. Phys. [4], vii. 318; Bull. Soc. Chim. 1866, ii. 11).

Dubrunfaut, by heating to redness a mixture of 1 at. sulphide of sodium and 1 at. chalk, obtained exactly 1 at. sodic carbonate and 1 at. calcic monosulphide, CaS.

Kolb treated in a soda-furnace two series of mixtures of chalk, carbon, and sodic sulphate, the first series being in the proportions corresponding to the equation of Dumas above given—the second corresponding to the equation:

$$Na^2SO^4 + CaCO^3 + C^4 = Na^2CO^3 + CaS + 4CO,$$

in which it will be observed that no oxide of calcium is formed. These two mixtures, when calcined and afterwards lixiviated under similar conditions, yielded exactly the same results. Hence Kolb concludes that the action of charcoal on a mixture of sodic sulphate and calcic carbonate in equal numbers of atoms yields sodic carbonate and calcic sulphide, easily separable by lixiviation at ordinary temperatures.

In this operation the reduction of the sodic sulphate by the carbon may be explained in two ways:

1. According to the ordinary theory, the exchange takes place as represented by the equation:

$$Na^2SO^4 + CaCO^3 = Na^2CO^3 + CaSO^4,$$

the carbon then acting on the calcic sulphate so as to reduce it to sulphide.

2. The charcoal may be supposed to exert a direct reducing action on the sodic sulphate, double decomposition then taking place between this compound and the calcic carbonate.

This latter view is confirmed by the experiments of Kolb, who finds that a mixture of sodic sulphate and chalk, calcined at a bright-red heat, yields nothing but sodic sulphate and quicklime.

The reduction of the sodic sulphate by charcoal might take place in two ways, viz.:

$$(1)\ Na^2SO^4 + C^4 = Na^2S + 4CO$$
$$(2)\ Na^2SO^4 + C^2 = Na^2S + 2CO^2.$$

But the composition of the gas evolved shows that the reaction takes place according to the second of these equations, and accordingly that the production of sodic carbonate should require the materials to be in the proportions deduced from the equation:

$$Na^2SO^4 + CaCO^3 + C^2 = Na^2CO^3 + CaS + 2CO^2.$$

But by actual experiment with these proportions in the soda-furnace, it is found that half the sodic sulphate remains unaltered, part of the charcoal being, in fact, employed in decomposing the chalk according to the well-known equation:

$$CaCO^3 + C = CaO + 2CO;$$

so that the action of the carbon is divided between the sodic sulphate and the chalk, in the manner shown by the equation:

$$Na^2SO^4 + CaCO^3 + C^3 = Na^2S + CaO + 2CO^2 + 2CO.$$

The chalk being decarbonised at the same time that the sodic sulphate is reduced, it follows that the carbonic acid of the chalk cannot contribute to the formation of the sodic carbonate. Kolb has in fact shown, by a series of analytical experiments, that the formation of sodic carbonate and calcic sulphide in the balling furnace is produced by the action of carbonic acid, parly resulting from the reduction of the sodic sulphide, partly existing in the gases of the furnace. Accordingly, when the mixture is heated in crucibles, so that it is not much exposed to the furnace-gases, a highly sulphuretted soda is obtained, whereas when it is heated in tubes traversed by a current of carbonic acid gas, a very pure sodic carbonate is obtained.

The temperature best adapted for the production of ball-soda is between the melting-point of bronze and of silver. Below the former, the reaction is incomplete; above the latter the soda is "burnt,"—that is to say, the sodic carbonate is decomposed, as shown by the following equation, yielding oxide and sulphide of sodium:

$$Na^2CO^3 + C = Na^2O + 2CO; \text{ and } Na^2O + CaS = Na^2S + CaO.$$

Kolb has also analysed a series of samples of ball-soda in the manufacture of which the coal had been replaced by wood-charcoal, peat, wood-shavings, &c. All these samples yielded similar results, whence it appears that the proportion of carbonaceous matter to be introduced into the mixture depends wholly upon its reducing power, which may be determined beforehand by an experiment with litharge.

The results show that the proportions required by theory are:

Sodic sulphate	100·0 parts
Chalk	70·4 „
Carbon	25·5 „

These proportions may, however, be considerably varied without sensibly affecting the result.

Action of Air and Water on Black Ash or Ball Soda (Kolb).—Dry air deprived of carbonic acid has no action on ball-soda, either at ordinary temperatures or at 100°; but at a red heat it converts the sulphide of calcium into sulphate, which in the subsequent lixiviation reconverts a certain portion of the sodic carbonate into sodic sulphate, and thereby diminishes the percentage of alkali in the product.

Carbonic anhydride in the dry state has no action on black ash (it does not act, indeed, either on lime or on sulphide of calcium); but in presence of moisture, it first converts the lime into carbonate, and then acts on the sulphide of calcium, forming carbonate and sulphydrate of calcium:

$$CaS + H^2O + CO^2 = CaCO^3 + H^2S; \text{ and } H^2S + CaS = CaH^2S^2.$$

When black ash is exposed to moist air, the lime contained in it is first hydrated by the aqueous vapour, and afterwards converted into carbonate. At the same time, any sulphide of sodium that may be present in the crude soda, is converted into hyposulphite, but the oxidation does not go any further. The sulphide of calcium, on the other hand, is oxidised by moist air, less quickly but more completely, being converted into calcic sulphate, which, as already observed, decomposes the sodic carbonate during lixiviation, and thereby diminishes the proportion of available alkali.

Another cause of the formation of calcic sulphate, and consequent deterioration of the ball-soda, is the presence of iron in the state of ferric oxide (not sulphide), which, in presence of moist air, reacts with the sulphide of calcium, forming lime and sulphide of iron, which latter becomes oxidised to sulphate; and this again in its turn reacts with the sulphide of calcium, forming ferrous sulphide and calcic sulphate:

$$Fe^2O^3.2SO^3 + 2CaS = 2FeS + 2CaSO^4 + O.$$

The same series of actions therefore recommences indefinitely, so that a very small quantity of ferric oxide is sufficient, under the influence of moist air, to convert a large quantity of calcic sulphide into sulphate. Hence the ball-soda should not be left exposed to the air longer than is necessary for the partial hydration of the lime contained in it, so as to facilitate its disintegration.

Action of Water.—By subjecting a given weight of ball-soda to the action of variable quantities of water for different times and at different temperatures, Kolb has obtained the following results:—

1. A given quantity of crude soda yields very different proportions of caustic soda and sodic sulphide, according to the quantity and temperature of the water with which it is treated, and the time of digestion.

2. The degree of causticity of the resulting solution is not sensibly affected by the quantity of water used, but increases with the time of digestion and with the temperature.

3. The proportion of sodic sulphide increases with the quantity of water, andmore particularly with the time of digestion and the temperature.

4. The decrease in the quantity of sodic carbonate not only corresponds with the quantity of caustic soda formed, but is also affected by the variation in the quantity of sodic sulphide: hence it would appear that the latter is formed at the expense of the carbonate.

5. The quantities of caustic soda and sodic sulphide do not appear to bear any definite relation to one another.

Kolb has likewise examined the action of water on pure sulphide of calcium, alone, and in presence of sodic carbonate, caustic soda, and lime. The results are as follows:

α. The quantity of calcic sulphide dissolved or decomposed by water is very small, but increases with the temperature and the duration of the digestion.

β. Lime has no sensible influence on the solubility of calcic sulphide; but a small quantity of caustic soda stops the solution almost entirely, especially at common temperatures.

γ. The decomposition of sodic carbonate by calcic sulphide: $Na^2CO^3 + CaS = Na^2S + CaCO^3$, which is considerable in very dilute liquids, diminishes on concentration, and ceases altogether in a solution saturated with sodic carbonate.

δ. The presence of caustic soda in small quantity (or, what comes to the same thing, of lime) prevents the action of calcic sulphide on sodic carbonate.

The accordance of these last results with the observed action of water on ball-soda affords a strong argument against the supposition that this substance contains an oxysulphide of calcium.

The following table exhibits the composition of black ash, as determined by different analysts. The arrangement of the basylous and acid elements in compounds is of course to a certain extent theoretical: thus, in the first three analyses, the oxide and sulphide of calcium are regarded as combined into an oxysulphide, whereas in the last three they are given separately:

Composition of Black Ash.

	Cassel.	*Glasgow.*	*Newcastle.*
	Unger.	Brown.	Richardson.
Sulphate of Sodium	1·99	1·16	3·64
Chloride of Sodium	2·54	1·91	0·60
Aluminate of Sodium	. .	2·35	
Carbonate of Sodium	23·57	35·64	9·89
Hydrate of Sodium	11·12	0·61	25·64
Lime	. .	6·30	
Carbonate of Calcium	12·90	29·17	15·67
Oxysulphide of Calcium	34·76	1·13	35·57
Sulphides of Iron	2·45	4·92	1·22
Silicate of Magnesium	4·74	3·74	0·88
Ultramarine	. .	0·29	
Carbon	1·59	8·00	4·28
Sand	2·02	4·28	0·44
Moisture	2·18	0·70	2·17
	99·86	100·20	100·00

	Liverpool.		
	Kynaston.	Murphy.	Muspratt and Danson.
Carbonate of Sodium	36·879	41·489	28·89
Chloride of Sodium	2·528	1·308	3·07
Sulphate of Sodium	0·395	0·748	0·82
Silicate of Sodium	1·182	1·162	8·27 caustic soda.
Aluminate of Sodium	0·689	0·392	0·40
Sulphide of Calcium	28·681	33·193	25·86
Carbonate of Calcium	3·315	0·857	14·22
Bisulphide of Calcium	0·435		
Hyposulphite of Calcium	1·152		
Sulphite of Calcium	2·178		
Caustic Lime	9·270	9·320	9·24
Magnesia	0·254	. .	2·03 as silicate.
Sulphide of Iron	0·371		
Ferric Oxide and Phosphate of Calcium	2·658	3·020	6·23
Alumina	1·132	1·020	
Charcoal	7·007	4·724	
Sand	0·901	2·259	
Ultramarine	0·959		
Moisture	0·219	. .	0·99
	100·205	99·492	100·02

SODA ALUM. $NaAl'''(SO^4)^2.12H^2O$.—Occurs native on the island of Milo, at the Solfatara near Naples, and near Mendoza, on the east of the Andes. (See SULPHATES.)

SODA COPPERAS. A sodio-ferric sulphate found in the alum-slate of Modum in Norway. (See SULPHATES.)

SODA SPODUMENE. Syn. with OLIGOCLASE (iv. 198).

SODA-LIME. A mixture of caustic soda and quick lime, used chiefly for nitrogen-determinations in organic analysis (i. 245).

SODALITE. A sodio-aluminic silicate, containing chlorine, occurring in dodecahedrons and other forms of the monometric system, with dodecahedral cleavage; sometimes in twin-crystals, having the form of a hexagonal prism, arising from the combination of two dodecahedrons; also massive. Hardness = 5·5—6. Specific gravity 2·26—2·37. Lustre vitreous, inclining to greasy. Colour grey, greenish, yellowish-white, and sometimes blue. Subtransparent—subtranslucent. Fracture conchoïdal—uneven. Before the blowpipe it melts to a colourless blistered glass.

Analyses (the chlorine being reckoned as chloride of sodium): *a.* From Vesuvius: colourless; specific gravity = 2·136 (Rammelsberg, Mineralch. p. 702).—*b.* From the same: green; very rare; small dodecahedrons with cubic faces, occurring in a limestone with vesuvian and nephelin.—*c.* Lamö near Brevig in Norway: blue, in elæolite (Bork, Pogg. Ann. lxxviii. 413).—*d.* From the Ilmen mountains near Miask: blue, in elæolite; specific gravity = 2·288 (E. Hofmann and G. Rose, *ibid.* xlvii. 377).—*e.* Lichfield, Maine: blue, in elæolite (Whitney, *ibid.* lxx. 431):

	a.	*b.*	*c.*	*d.*	*e.*
Silica . .	38·12	38·76	38·86	38·40	37·46
Alumina . .	31·68	34·62	30·82	32·04	30·93
Lime (and MgO)	. .	. .	1·65	0·32	
Soda . . .	18·49	21·18	16·39 *	18·24	18·33
Potash					
Sodium . .	4·37	1·67	4·57	4·63	4·55
Chlorine . .	6·69	2·55	7·00 †	7·10	6·97
	99·35	98·78	99·29	100·73	98·24

These analyses may be represented by the formula $NaCl.n(NaAl'''SiO^4)$. (compare the formula of haüyne, iii. 15), the sodium-chloride and the silicate being crystallised together isomorphously in varying proportions.

Sodalite occurs in mica-slate, granite, trap, basalt, and volcanic rocks. In Greenland it is found in mica-slate, together with felspar, hornblende and eudialyte.

SODAMIDE. *Olive-coloured Sodium-compound.*—When a quantity of sodium which evolves from water 100 measures of hydrogen gas, is heated in ammoniacal gas, it absorbs tranquilly between 142 and 163 measures, setting 100 measures of hydrogen free, and assuming first a blue and afterwards a green colour. The compound is olive-green and fusible, and manifests the same relations as the corresponding potassium-compound (iv. 695). (Gay-Lussac and Thénard, *Recherches*, i. 354; H. Davy, *Phil. Trans.* 1810, p. 24.)

Sodamide appears to be capable of uniting with sodic oxide. When a mixture of oxygen and ammonia gases, the latter being in excess, is passed over sodium, sodamide alone is formed, and at a lower temperature than with pure ammonia gas; but if the quantity of oxygen is increased, a fused ruby-coloured mass is obtained, consisting of a compound of sodic amide and oxide. This compound is permanent in ammonia gas, even at 300°, but becomes decolorised when air or oxygen is passed over it, and leaves a white substance, apparently consisting of sodic hydrate.—*Potassium* treated in like manner yields a similar compound, but of a deep blue colour. (Weyl.)

SODAMMONIUM. NH^3Na, or rather $N^2H^6Na^2$? (Weyl, Pogg. Ann. cxxi. 697; Jahresb. 1864, p. 163.)—This compound appears to be formed when lumps of pure bright sodium are placed at one end of a bent tube, a quantity of silver-chloride previously saturated with ammonia gas at the other, the tube then sealed, the end containing the silver-chloride heated in a chloride-of-calcium-bath, and the other end immersed in cold water. The sodium then swells up, and is converted into a liquid, which is copper-red by perpendicularly reflected, greenish-yellow by obliquely reflected light, blue in thin films by transmitted light. As the silver-chloride cools, and the ammonia gas is reabsorbed, the sodammonium decomposes and pure sodium remains behind, having a dull surface and spongy texture. By again heating the silver-chloride the compound may be reproduced any number of times.

A *sodammonium-amalgam* appears to be formed by exposing in like manner to the action of ammonia gas, a pulverulent amalgam of nearly equal parts of sodium and mercury. After two hours' action, the portion of the mass in contact with the surface of the tube exhibits a metallic lustre and bronze-red colour, while the interior is dull and brick-red. This product can likewise exist only in an atmosphere of ammonia, being resolved in a few hours after the cooling of the silver-chloride, into ammonia, free mercury, and a sodium-amalgam containing less mercury than the original amalgam.

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* Including 0·51 potash.

† By difference.

Potassammonium, $N^2H^6K^2$?, is prepared like sodammonium, and exhibits similar properties.

Other metallammoniums may be produced by the decomposition of sodium- or potassammonium. Thus when a mixture of a metallic chloride or oxide with an equivalent quantity of sodium is exposed in the manner above described to the action of ammonia-gas, the gas is first absorbed by the metallic chloride (or oxide) and afterwards by the sodium, the sodammonium thus formed flowing over the metallic salt, and reacting upon it without much rise of temperature, With a mixture of barium-chloride and sodium the reaction appears to be:

$$\underset{\text{Sodammonium.}}{N^2H^6Na} + 2NH^3 + Ba''Cl^2 = \underset{\text{Barammonium.}}{N^2H^6Ba''} + \underset{\text{Chloride of Sodammonium.}}{2NH^3NaCl.}$$

Barammonium forms a deep blue liquid having a metallic lustre.—*Copper-*, *Mercury-*, and *Silver-ammonium* are obtained in like manner from the respective chlorides, and *zinc-ammonium* from the oxide. These compounds are likewise very unstable, being resolved, even in the sealed tube, into metal (which appears grey, dull and destitute of coherence) and ammonia. If in the arrangement just described the metallic chloride be replaced by an ammonium-salt, *e.g.* NH^4Cl or $(NH^4)^2SO^4$, similar reactions take place, and the tube becomes filled with a blue liquid mixed with excess of ammonia. This blue liquid, which is also formed by the action of potassic hydrate on potassammonium, appears to consist of *ammonium* itself, N^2H^8. It is even more unstable than the metallammoniums, being resolved into ammonia and hydrogen, partly even before the reaction between the ammonium-salt and the sodammonium is completed.

Tetrasodammonium. NNa^4?—Monosulphide of sodium brought in contact, in a sealed tube, with liquid ammonia, is converted (with transient formation of liquid ammonium) into an orange-yellow substance, which soon decomposes, leaving a white substance still containing ammonia. This residue gives off ammonia on exposure to the air, and the odour of ammonium-sulphide when heated. It is perhaps formed in the manner represented by the equation:

$$4Na^2S + 8NH^3 = (NNa^4)^2S + 3(NH^4)^2S.$$

Tetrapotassammonium appears to be formed in a similar manner. (Weyl.)

SODIUM. *Atomic Weight* 23. *Symbol* Na (from *Natrium*). Soda, the alkali containing this element, was formerly confounded with potash, but was proved to be a distinct substance by Duhamel in 1736, and subsequently by Marggraf in 1758. H. Davy first obtained the metal in the year 1807.

Sodium is a very abundant element and very widely diffused. It occurs in large quantities, as chloride, in rock-salt, sea-water, salt-springs, and many other mineral waters; abundantly also as nitrate, forming beds several feet thick on the dry pampas of Peru; more rarely as carbonate, borate, and sulphate, either in springs, lakes, &c., or in the solid state; as sodio-aluminic fluoride in cryolite; and as silicate combined with earthy silicates in chabasite, analcime, natrolite, thomsonite, eudialite, albite, soda-spodumene, labrador, nepheline, hauyne, sodalite, brewicite, cancrinite, and achmite; in very small quantity also in bole, pitchstone, pumice-stone, obsidian, ittnerite, and pinite. Traces of sodium-salts are found in coal, in all kinds of limestone and dolomite, and in talc, asbestos, and other minerals. In the vegetable kingdom it occurs as sulphate, iodide, and chloride, and combined with vegetable acids, especially in plants growing in or near the sea; in the animal kingdom, combined with carbonic, phosphoric, sulphuric, hydrochloric, and various organic acids.

Preparation of the Metal. The preparation of sodium is similar to that of potassium. Davy first obtained it by the electrolysis of the hydrate; Gay-Lussac and Thénard afterwards prepared it by decomposing that compound with metallic iron at a white heat; and Brunner showed that it may be prepared with much greater facility by distilling a mixture of sodic carbonate and charcoal.

The preparation of sodium by this last-mentioned process is much easier than that of potassium, not being complicated, or only to a slight extent, by the formation of secondary products. Within the last few years it has been considerably improved by Deville and others, and carried out on the manufacturing scale, sodium being now employed in considerable quantity as a reducing agent, especially in the manufacture of aluminium and magnesium and in the silver amalgamation process (p. 285).

The sodic carbonate used for the preparation is prepared by calcining the crystallised neutral carbonate. It must be thoroughly dried, then pounded, and mixed with a slight excess of pounded charcoal or coal. An inactive substance, viz. pounded chalk, is also added to keep the mixture in a pasty condition during the operation, and prevent the fused sodic carbonate from separating from the charcoal. The following are the proportions recommended by Deville:

For Laboratory Operations.		*For Manufacturing Operations.*	
Dry sodic carbonate	717 parts	Dry sodic carbonate	30 kilogr.
Charcoal	175 „	Coal	13 „
Chalk	108 „	Chalk	3 „

These materials must be very intimately mixed by pounding and sifting, and it is advantageous to calcine the mixture before introducing it into the distilling apparatus, provided the calcination can be effected by the waste heat of a furnace; the mixture is thereby rendered more compact, so that a much larger quantity can be introduced into a vessel of given size.

The distillation is performed, on the laboratory scale, in a mercury bottle heated exactly in the manner described for the preparation of potassium.

For manufacturing operations, the mixture is introduced into iron cylinders, which are heated in a reverberatory furnace, and so arranged that, at the end of the distillation, the exhausted charge may be withdrawn and a fresh charge introduced without displacing the cylinders or putting out the fire. The receivers used in either case are exactly the same in form and dimensions as those employed in the preparation of potassium (iv. 693).

When the process goes on well, the sodium collected in the receivers is for the most part perfectly pure, the carbonised products which give so much trouble in the preparation of potassium being produced in very small quantity only, if at all. Nevertheless a small quantity of somewhat impure sodium always remains attached to the inner surface of the receivers; hence when a receiver has been used, the plates should be separated and scraped before they are used again; and the matter scraped off, being received under naphtha, may be collected after a while and will yield by distillation a considerable quantity of sodium. Lastly, the pure metal obtained by this and by the first distillation is melted under a thin layer of naphtha, which is decanted as soon as the sodium becomes perfectly fluid, and the metal is then run into moulds like those used for casting lead or zinc.

The degree of heat absolutely required for the reduction of sodium is not much higher than for the reduction of zinc; but the distillation goes on better and a larger product is obtained when the temperature is raised considerably higher. The quantity of sodium obtained in a well conducted operation, is about one-third of the weight of the calcined mixture.

[For a detailed description of the manufacture of sodium, with figures of the apparatus, see *Chemical Technology*, i. [4], 5 and [5], 125.]

Properties.—Sodium has a high lustre, and usually a silver-white colour; according to Long however (Chem. Soc. Q. J. xiii. 123), its surface when perfectly clean and metallic, is of a beautiful rose colour, which is best seen when a ray of light falling on a surface of the metal is reflected back from a second surface and again reflected from the first.

The specific gravity of sodium is 0·9348 (Davy); 0·97223 at 15° (Gay-Lussac and Thénard); 0·985, reduced to a vacuum and compared with that of water at 3·9 (Schröder, Jahresb. 1859, p. 12). It is rather hard at − 20°, very ductile at 0°, of the consistence of wax at common temperatures, semifluid at 50°: melts completely at 97·6° (Regnault, Jahresb. 1856, p. 43), at 95·6° (Bunsen, *ibid.* 1863, p. 178). When a few grammes of sodium are melted in a sealed tube filled with coal gas, then left to cool till a few solid points appear on the surface, and the remaining liquid suddenly poured off by inclining the tube, the solidified portion remains in shining octahedral crystals belonging to the dimetric system and having the plane angles at the apex = 50° (Long). Sodium is less volatile than potassium (Davy; Gay-Lussac and Thénard); rather more so (Mitscherlich). Its vapour is colourless. Sodium is an excellent conductor of heat and electricity.

Sodium when exposed to the air oxidises like potassium, but not quite so rapidly. When heated in the air it burns with a yellowish flame, forming protoxide and dioxide of sodium. When heated in oxygen gas till it no longer increases in weight, it is wholly converted into dioxide. When dropt upon cold water, it decomposes a portion of the water, liberating hydrogen and running about on the surface with a hissing noise, but the gas does not take fire unless the water be previously heated.

Sodium is a monatomic metal belonging to the group which includes the other alkali-metals and silver. With chlorine, bromine, iodine and fluorine, it forms the compounds KCl. KBr, &c.; with oxygen it forms a protoxide Na_2O, the corresponding hydrate

NaHO, and a dioxide Na^2O^2; with sulphur, a protosulphide Na^2S, a sulphydrate NaHS, and several polysulphides.

SODIUM, ALLOYS OF. These alloys closely resemble those of potassium, and are prepared in like manner by fusing sodium with the respective metals. The *amalgam of sodium* (iii. 889) is much used as a reducing or hydrogenating agent. M. Scholz (J. pr. Chem. lxxix. 441), by adding sodium to mercury in such quantity that the product solidifies completely on cooling, then pressing out the excess of mercury, fusing the remaining amalgam, and leaving it to cool slowly, obtains a sodium-amalgam, crystallised in fine prisms, often an inch long, which may be kept in well closed vessels without sensible oxidisation, and are easily pulverised. By further addition of mercury, this amalgam may be brought to a more or less fluid state.—F. Muhlhäuser (Zeitschr. Ch. Pharm. 1864, p. 720) heats sodium under naphtha to 90°, and allows mercury to flow into it in a fine stream. The sodium then swells up and ultimately forms a solid mass, which may be left to cool under naphtha.

Respecting the alloys of potassium and sodium, see POTASSIUM (iv. 695).

SODIUM, ANTIMONIDE OF. Prepared by direct combination of its elements. Resembles antimonide of potassium (i. 317).

SODIUM, ARSENIDE OF. This alloy, which is used for the preparation of the arsenides of ethyl, methyl, &c., is prepared by gently heating finely pulverised metallic arsenic in a furnace having a good draught till it begins to fume, and then introducing small pieces of sodium from time to time till the mixture begins to assume a fluid consistence, which effect takes place when a quantity of sodium has been introduced about equal to that of the arsenic. As the product is highly combustible it is necessary to exclude the air, for which purpose the arsenic is placed in a porcelain crucible enclosed within a hessian crucible, both being provided with closely fitting covers, which must only be removed to introduce the sodium, or to stir the mixture with an iron rod. The action is very violent and attended with vivid incandescence. The alloy, which has a crystalline fracture and silver-white colour, must be kept in closely stoppered bottles filled up with sand. It decomposes water with evolution of arsenetted hydrogen, an effect which takes place even in damp air: hence it must be handled with caution. (Landolt, Ann. Ch. Pharm. lxxxix. 201.)

SODIUM, BROMIDE OF. NaBr. This salt, produced by saturating hydrobromic acid with soda, or by decomposing ferrous bromide with sodic carbonate, crystallises by evaporation at temperatures above 30°, in anhydrous cubes, at lower temperatures in oblique rhombic prisms containing $NaBr.2H^2O$ (Mitscherlich). The specific gravity of the anhydrous salt referred to water at 17·5° as unity is 3·079 (Kremers, Jahresb. 1857, p. 69). It dissolves easily in water and in alcohol. The following table exhibits the specific gravities and expansions by heat of solutions of various strengths. (Kremers, Jahresb. 1858, 41.)

Volumes of Aqueous Bromide of Sodium at different temperatures (vol. at 19·5° = 1).

Quantity of salt in 100 parts of water	20·4	42·6	62·3	88·1
Specific gravity of solution at 19·5°.	1·1450	1·2826	1·3885	1·5096
0°	0·99380	0·99189	0·99067	
19·5	1·00000	1·00000	1·00000	1·00000
40	1·00852	1·00980	1·01032	1·01076
60	1·01858	1·02832	1·02108	1·02164
80	1·03021	1·03178	1·03249	1·03298
100	1·04347	1·04421	1·04453	1·04477

A saturated aqueous solution boils at 121°. (Kremers.)

SODIUM, CHLORIDE OF. NaCl. *Common salt, Culinary salt, Rock-salt, Sea-salt*, formerly called *Muriate of Soda*. This compound is formed by the direct union of its elements, sodium taking fire in chlorine gas. It may likewise be obtained pure by neutralising hydrochloric acid with soda or sodic carbonate and evaporating. It occurs very abundantly in nature, both in the solid state, as rock-salt, forming extensive beds in rocks of various ages,—and in solution in sea-water, salt-lakes, and brine-springs; in smaller proportion also in river water.

In Europe common salt usually occurs in the new red sandstone, or associated with red marl, but it is not confined to those rocks. In Durham, Northumberland, and Leicestershire, salt-springs arise from the carboniferous series; in the Alps, some saltworks are supplied from oolitic rocks: the extensive mines of Cardona in Spain are referred to the greensand formation, those of Wieliczka in Poland to tertiary rocks. Salt-springs occur also in volcanic regions. In the United States the brine comes mostly from Silurian sandstones. Salt occurs also as efflorescences over the dry prairies of the Rocky mountains and California; and in most desert and semi-desert regions there are numerous salt lakes.

The principal salt mines of Europe are at Wieliczka in Poland; at Hall in the Tyrol, and along the range through Reichenthal in Bavaria, Hallein in Salzburg, Halstadt, Ischl and Ebensee in Upper Austria, and Aussee in Styria; at Stassfürth near Magdeburg; in Hungary at Marmoros and elsewhere; in Transylvania, Wallachia, Gallicia and Upper Silesia; at Vic and Dreuze in France; in the valley of Cardona and elsewhere in Spain; at Bex in Switzerland; at Northwich and elsewhere in Cheshire; and near Belfast in the north of Ireland. At Wieliczka the salt deposit is 500 miles long, 20 miles broad, and not less than 1200 feet thick; at Cardona, the salt forms hills 300 and 400 feet high. Near Northwich, the principal deposit of rock-salt in England, the mineral occurs in magnesian limestone, in two beds situated one above the other, separated by about 30 feet of clay and marl, intersected by small veins of salt, the two beds together being about 60 feet thick, 300 yards broad, and a mile and a half long.

Rock-salt occurs also near lake Oroomiah, the Caspian, &c., forming hills and extended plains; in Algeria abundantly; in Abyssinia; in India, in the province of Lahore, and the valley of Cashmere; in Scinde, where there is said to be an immense bed of it, 20 miles long, 15 miles broad, and averaging three feet in thickness; in China and Asiatic Russia; in Peru and other countries of South America. In the United States salt has been found forming beds with gypsum in Washington county, Virginia, and in the mountains of Oregon. (Dana, ii. 9).

The mode in which salt is obtained from these deposits depends very much on the locality, the depth of the deposit, the price of fuel, &c. In some places, as at Wieliczka and in Cheshire, it is a mining operation and is carried on by means of shafts and horizontal galleries. At Cardona in Spain, where the great body of the salt forms a rugged precipice 400 to 500 feet high, there is no excavation, but the salt is procured by working down perpendicularly as in an open quarry.

Analyses of Rock-salt.

	Wielicska.	Berchtesgraden.	Hall, Tyrol.	Hallstadt, Austria.	Schwäbisc, Hall.	Wilhelmsglück.	Vic.
Chloride of Sodium	100·00	99·85	99·43	98·14	99·63	98·36	99·30
„ Potassium	. .	trace	trace	trace			
„ Calcium	. .	trace	0·25	. .	0·09		
„ Magnesium	trace	0·15	0·12	. .	0·28		
Sulphate of Sodium	. .	. .	. .	. .	. .	0·03	
„ Calcium	. .	. .	0·20	1·86	. .	0·55	0·50
Carbonate of Calcium	. .	. .	. .	. .	. .	0·52	
„ Magnesium	. .	. .	. .	. .	. .	0·13	
Clay, Ferric oxide, and other insoluble matter	. .	. .	. .	. .	. .	0·53	0·20
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

	Algeria.			Holsten, U. S.	Boring at Stassfürth.		Cheshire.	Cardona.
	Djebel Merah.	Ouled Kebbah.						
		fibrous.	impure.					
Chloride of Sodium	97·0	98·89	72·16	99·55	94·57	25·09	98·30	98·55
„ Calcium	. .	. .	1·65	trace	. .	. .	. .	0·99
„ Magnesium	. .	1·11	5·57	. .	0·97	. .	0·05	0·02
Sulphate of Sodium	. .	. .	. .	. .	. .	1·57		
„ Calcium	3·0	. .	10·72	. .	0·89	1·23	1·65	0·44
„ Magnesium	. .	. .	2·06	. .	. .	42·07		
Carbonate of Calcium	. .	. .	3·71					
„ Magnesium	. .	. .	2·89	0·45				
Clay, Ferric oxide, &c.	. .	. .	1·24	. .	3·35	1·83		
Water . . .	. .	. .	. .	. .	0·22	28·21		
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Rock-salt is sometimes so pure and white that it requires no preparation but grinding to convert it into snow-white culinary salt; this is the case with the salt of Cardona, and with some of that occurring in Cheshire and other localities. More frequently, however, it is coloured red or brown from the admixture of clay or bitumen, and particularly of the kind of infusoria that are now found inhabiting salt lakes: it then requires to be purified by solution and recrystallisation. Frequently also, instead of sinking a shaft to the bed of salt and mining it, the superior strata are pierced by a bore only a few inches in diameter, by which water is admitted to the bed, and the brine formed is drawn off by a pump.

Salt wells or springs, which may be artificially constructed in the manner above described, are also frequently found ready formed in nature wherever a spring during its course has come in contact with a bed of rock-salt. These however are rarely so highly saturated as the artificial wells, although this is actually the case with that of Luneburg, which contains 25 per cent. of saline matter; but they are for the most part, only slightly impregnated, or have become weakened by subsequent addition of fresh water. This difference in the strength and the composition of the saline constituents of salt springs may be seen from the following table (p. 334).

The water of the stronger springs is at once evaporated by heat to procure the salt, and in England and other countries where cheap fuel can be obtained, the same plan is adopted with the weaker springs; but in Germany, where fuel is scarce and dear, the more dilute saline waters cannot be profitably worked in this way. The water is therefore first concentrated by a process called *graduation*, which consists in exposing the brine, diffused over a large surface, to the air. This is effected by pumping it to a height, and then allowing it to trickle slowly over large stacks of faggots, piled in suitable buildings, screened from rain, but freely exposed to the prevailing wind. After this process has been repeated eight or ten times, the solution acquires a density of about 1·40, and is sufficiently concentrated to allow the evaporation to be finished by heat. In the first evaporating pan an insoluble double sulphate of calcium and sodium is deposited, partly in the form of mud or *schlot*, as it is called in Germany, partly as a hard scale, which adheres to the bottom of the pans (*Pfannenstein*). A specimen of this panstone from Schönebeck gave by analysis:

$NaCl$.	Na^2SO^4.	K^2SO^4.	$CaSO^4$.	$MgSO^4$.	$MgCO^3$.	Al^2O^3 and Fe^2O^3.	SiO^2.	H^2O.
44·28	20·67	2·13	27·38	1·64	0·41	0·03	0·02	3·44 = 100

When the liquor reaches a density of 1·236 it is decanted into another pan and evaporated, the crusts of salts being removed as they form.

The appearance of the salt varies according to the rate at which the evaporation is conducted. When the brine is boiled down rapidly, it furnishes the mealy fine-grained salt used for the table; slower evaporation yields the hard crystallised salt, generally used for salting fish.

Separation of Salt from Sea-water.—It is seldom that artificial evaporation is employed for separating the salt from sea-water; where it is practised, the same mode is adopted as with the brine springs; sometimes, as in Siberia, frost is made subservient to this object—for salt water separates on freezing into ice (containing no salt), and a strong saline ley. Dr. Kane states that if the cold is sufficiently intense, the water which is obtained on melting the ice is fit for drinking. This plan is pursued in Prussia, Sweden, and other northern countries, where the sea-water is frozen in reservoirs, and the concentrated brine liquor is boiled down to salt. The salt obtained by this plan, however, is not pure, as the following analyses by Hess will prove.

Constituents.	Irkowtsk.	Selenguisk.	Oustkoutsk.	Okhotzk.		
				1st crystallisation.	2nd crystallisation.	3rd crystallisation.
Chloride of Sodium	91·5	74·7	76·3	86·0	77·6	79·1
„ Aluminium	2·6	6·5	1·2	3·6	6·2	7·8
„ Calcium	1·1	1·4	3·8	0·9	0·9	0·7
„ Magnesium	2·0	3·6	3·6	2·0	1·7	0·8
Sulphate of Sodium	2·8	13·8	12·6	7·5	13·6	11·6
„ Calcium	. .	. .	2·5			
	100·0	100·0	100·0	100·0	100·0	100·0

The evaporation of sea-water is effected wholly or partly by the influence of the air and sun, in what are termed in some localities *Salterns* or *Brine-pans*. Hayling Island, near Portsmouth, has been celebrated for many centuries for its manufacture of salt, carried on in this way during the summer months. The brine-pans vary in size up to a quarter of an acre, in which, in favourable weather, the sea-water becomes brine in about seven days. It is then pumped by windmills into reservoirs or pits, whence it is run into sheet-iron pans, and is boiled for twelve hours, during which

Analyses of the SSalts from Saline and Brine Springs.

Locality	Halle.	Schöne-beck.	Artern.	Dürren-berg.	Kösen.	Neu Salzwerk.	Sulza.	Nau-heim.	Soden.	Clemens-hall.	Reichen-hall.	Kissin-gen.	Cheltenham.			Caledonia, Canada.	Tarentum, U. States.
Per cent. of salt in water .	19·28	11·10	26·50	8·39	4·96	4·25	4·39	2·87	1·27	26·39	23·30	1·04	0·92	0·82	1·06	7·64	4·09
Chloride of Sodium . .	94·43	93·72	95·35	89·88	87·60	80·80	91·24	82·23	86·01	98·17	96·99	75·30	74·53	53·08	80·90	84·31	78·24
,, Potassium .	0·21	. .	0·45	. .	. .	. .	0·72	1 83	1·81	. .	. .	0·62	. .	. .	. .	0·39	
,, Calcium . .	1·03	. .	. .	. .	. .	. .	. .	6·74	. .	. .	. .	. .	. .	. .	. .	. .	13·66
,, Magnesium .	1 69	0·67	1·59	1·49	. .	0·65	. .	1·18	2·24	trace	0·20	6·85	. .	. .	. .	. .	7·17
,, Barium . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·93
,, Ammonium .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·01						
Bromide of Sodium . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·51	. .	. .	KBr 0·22	trace
,, Calcium . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·35			
,, Magnesium .	. .	. .	. .	. .	. .	0·008	. .	0·04	. .	. .	0·01	0·63	. .	. .	0·41		
Iodide of Sodium . . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·02	
,, Magnesium . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·06		
Sulphate of Potassium . .	. .	1·34	1·10	0·99	0·62	0·11	. .	. .	. .	. .	0·26	. .	0·46	. .	. .	0 06	
,, Sodium . .	. .	. .	. .	. .	0·57	. .	2·53	. .	. .	0·08	. .	. .	17·48	25·19	11·19		
,, Calcium . .	2·23	2·55	1·51	0·04	8·83	7·04	3·38	0·18	0·65	1·68	1·79	3·13	. .	1 99			
,, Magnesium .	. .	1·18	. .	0·63	2·08	6·93	0·78	. .	. .	. .	0·73	1·60	. .	11·33	1·37		
,, Aluminium .	. .	. .	. .	6·77													
Carbonate of Sodium . .	0·37	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	3·13	. .	. .	2·31	
,, Calcium . .	. .	0·44	. .	0 15	0·28	2·52	0·40	7·43	7·73	0·07	0·004	9·37	1·19	3·96	2·30	1·54	
,, Magnesium .	. .	0·05	. .	0·02	trace	1·67	. .	. .	0·77	. .	trace	1·88	1·76	0 34	0·92	6 77	
,, Iron. . .	0·02	0·03	. .	. .	. .	0·16	0 95	0·23	0·29	. .	0·003	0·62					
,, Manganese .	. .	. .	. .	. .	. .	0·002	. .	0·07									
Silicate of Sodium . .	. .	. .	. .	. .	. .	. .	. .	. .	0·50								
Phosphate of Iron . .																	
Oxide of Iron . . .	. .	. .	. .	0·01	0·02												
,, Manganese . .																	
Alumina	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	trace	
Silica	. .	0·02	. .	0·02	. .	0·11	. .	0·07	. .	. .	0·005	. .	0·43	0·18	0·37	0·56	
Organic matter . . .	0·02	. .	. .														
Crenic acid	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	0·51	2 94	2·48		
Carbonic acid . . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	3·82	
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·002	100·00	100·00	97·26	100·00	100·00	100·00

it is skimmed to remove impurities. The crystals of salt begin to appear towards the end of the day, and are shovelled out, hot and wet, into wooden troughs with holes in the bottom to allow the *Litters* to run off.

A somewhat similar plan is pursued at Lymington in Hampshire, but the brine is there run through a series of salterns before it is pumped into the boiling-pans. The drainings from the troughs drop on upright stakes of wood, on which stalactitic masses accumulate in ten or twelve days, weighing from 60 to 80 lbs.; these masses are called *Salt cats*. The residual liquor called *Bitters*, *Bittern*, or *Bittern liquor*, is employed in the manufacture of the carbonate or sulphate of magnesium.

For many centuries salt was also obtained from sea-water in the Firth of Forth and other places on the east coast of this country, by evaporating it in large shallow iron pans, salt works of this kind in former days being given as donations to abbeys.

In warmer latitudes, as on the shores of the Mediterranean, the evaporation is carried on entirely under the influence of the sun and air in a series of shallow ponds, called *salt-gardens*, in which the water is spread over a very large surface. As the evaporation goes on, salt is deposited in the pools farthest from the sea, while the nearer ones are constantly receiving fresh supplies of salt water.

In the salt works of the Mediterranean, the greater part of the surface is about a foot below the main level of the sea. The ponds are divided by small banks of earth two feet high and from one to two feet thick. The salt water is admitted by a small flood-gate and circulates by means of openings in the banks. It enters with a density of 1·025, and continues to increase in density by evaporation under the influence of the dry winds, until it attains a density of 1·143. Its volume is then reduced to one-sixth of its first proportions. It now begins to deposit sulphate of calcium, till the density reaches 1·210. It is then conveyed by means of pumps, worked by horse or steam power, to reservoirs slightly more elevated, the bottoms of which are generally composed of hard clay well beaten in, where the precipitation of the salt takes place. The volume is by this time reduced to one-tenth of its original bulk. From the density of 1·210, representing 25° on Beaumé's hydrometer, up to 1·286, equal to 32° on the same scale, the evaporation takes place in the open air, the liquid constantly depositing chloride of sodium almost pure, which goes into the market without further preparation. In order to obtain it care is taken to run off the liquor marking 32° B., which covers the bed of salt about two inches thick. It is then collected by means of shovels, and thrown into heaps called in the south of France *Caniells*, and in Italy *Cumuli*. It is then allowed to drain, after which it is ready for sale. The salt thus obtained is called bay-salt.

The mother-liquor or bittern is used as a source of bromine. It also contains considerable quantities of sulphate of sodium, and of the sulphates and chlorides of magnesium and potassium. The mode of treating it so as to obtain these salts, especially the chloride of potassium, has been brought to great perfection by Balard. (See POTASSIUM-SALTS, iv. 717, also SULPHATES.)

The following table shows the nature and amount of the impurities in several kinds of commercial salt.

Analyses of Common Salt.

	Schönebeck.	Stassfurth.	Dürrenberg.	Ludwigshall.	Cheshire. *stoved.*	Lymington. *Cat-salt.*	St. Malo. *Sea-salt.*	St. Uber. *Sea-salt.*	Cadiz. *Sea-salt.*
Chloride of Sodium .	95·402	97·094	96·061	99·45	98·250	98·80	96·00	89·04	
" Calcium .	. .	. .	. .	. .	0·025				
" Magnesium	0·080	0·345	0·213	. .	0·075	0·50	0·30	2·38	
Sulphate of Sodium .	. .	. .	. .	0·05	. .	. .	. .	1·44	0·99
" Potassium .	0·414	0·390	. .	. .	. .	. .	. .	trace	trace
" Calcium .	0·732	0·727	1·277	0·28	1·550	0·10	2·35	0·98	0·33
" Magnesium	0·471	0·180	0·279	. .	. .	0·50	0·45		
Silicate of Sodium .	. .	. .	. .	. .	. .	. .	. .	0·02	trace
Nitrate of Sodium .	. .	. .	. .	. .	. .	. .	. .	trace	
Insol. matter, ferric oxide, alumina, &c.	. .	. .	0·015	. .	. .	. .	. .	0·28	0·27
Water . . .	2·901	1·264	2·155	. .	. .	. .	. .	6·10	6·30
	100·000	100·000	100·000	100·000	99·900	99·90	99·10	100·25	100·34

Properties.—Pure chloride of sodium has an agreeable saline taste. It crystallises from aqueous solution by evaporation at ordinary or higher temperatures, in colourless transparent cubes, which are anhydrous. Rock-salt is often found crystallised in cubes, octahedrons, and intermediate forms, and occasionally in tetrakis-hexahedrons (ii. 127); it exhibits perfect cubic cleavage. Specific gravity 2·1—2·57. Hardness = 2·5. It often occurs in large crystalline, transparent, and colourless masses, possessing perfect diathermancy, that is to say, it is equally pervious to heat-rays of every degree of refrangibility (p. 61). An aqueous solution of sodic chloride exposed to a temperature of about −10° deposits the salt in hexagonal plates containing $NaCl.2H^2O$; but as the temperature rises, the water of crystallisation is expelled, and the crystals fall to pieces, being converted into a heap of minute cubes. The anhydrous salt, when rapidly crystallised, contains mechanically enclosed water, and consequently decrepitates in the fire. Some specimens of rock-salt from Wieliczka decrepitate when thrown into water, owing to the escape of condensed gas, consisting, according to H. Rose, of CH^4.

Chloride of sodium melts at a red heat, and forms a crystalline mass on cooling. It is somewhat less volatile than chloride of potassium, but like that salt, volatilises at a low red heat in open, but not in covered, vessels (**H. Rose**); at a white heat it volatilises, even in closed vessels. Heated with potassium, it yields chloride of potassium, and metallic sodium (**Davy**). When heated to redness with silica, it yields silicate of sodium and hydrochloric acid gas, the decomposition taking place rapidly in presence of aqueous vapour. With oil of vitriol it gives sulphate of sodium and hydrochloric acid gas. According to Berthollet, it also evolves a small quantity of hydrochloric acid gas by distillation with oxalic acid, but not with acetic acid. In solution it is decomposed by excess of lead-oxide, into soda and subchloride of lead, Pb^2Cl^2 (**Scheele**), also by nitrate of ammonia. (**Karsten.**)

Anhydrous chloride of sodium dissolves in about 3 pts. of cold water, and is scarcely more soluble in boiling water. Fuchs states that 100 pts. of water dissolve 37 pts. of it at all temperatures; but, according to Gay-Lussac and Poggiale, the solubility increases slightly with rise of temperature, as shown by the following table:

			Poggiale.	Gay-Lussac.	
100 parts of water at	0°	dissolve of NaCl	35·52		parts
„ „	14	„	35·87		„
„ „	$14\frac{4}{5}$	„	. .	36	„
„ „	60	„	. .	37	„
„ „	100	„	36·61		
„ „	$107\frac{3}{5}$	„	. .	40·38	„
„ „	110	„	40·35		

The specific gravity of the solution increases with its strength as follows (**Gerlach**, Jahresb. 1859, p. 43):

Quantity of NaCl in 100 pts. of solution.	5	10	15	20	25	26·395
Specific gravity of solution at 15°.	1·0362	1·0734	1·1115	1·1511	1·1923	1·2043

The number 26·395 represents the quantity of anhydrous sodium-chloride in a saturated solution at 15°. For an extended table by Gerlach of the specific gravities of salt-solutions of various strengths and at various temperatures from 0° to 100°, see *Chemical Technology*, vol. i. part 5. See also **Schiff** (Jahresb. 1858, p. 39); and **W. Schmidt** (*ibid.* 1859, p. 128).

The following determinations of the variations in volume of salt-solutions at different temperatures are by **Kremers** (Jahresb. 1857, p. 68):

Volumes of Aqueous Chloride of Sodium at different temperatures (vol. at 19·5° = 1).

Quantity of salt in 100 p.s. water.	4·7	10·0	15·4	20·5	25·8	31·4
0°	0·99639	0·99175	0·99371			
10	0·99783	0·99715	0·99674	0·99641	0·99620	0·99604
19·5	1·00000	1·00000	1·00000	1·00000	1·00000	1·00000
30	1·00327	1·00381	1·00410	1·00435	1·00456	1·00464
40	1·00710	1·00790	1·00840	1·00878	1·00910	1·00928
50	1·00150	1·01246	1·01309	1·01353	1·01391	1·01412
60	1·01646	1·01748	1·01817	1·01860	1·01898	1·01919
70	1·02201	1·02303	1·02364	1·02400	1·02431	1·02454
80	1·02809	1·02889	1·02945	1·02971	1·02993	1·03006
90	1·03466	1·03524	1·03560	1·03576	1·03581	1·03591
100	1·04179	1·04209	1·04217	1·04214	1·04211	1·04190

The freezing and boiling-points of the solution rise with the degree of concentration in the manner shown in the following table (Karsten):—

Per cent. of salt	1	5	10	15	20	25	29
Freezing-point .	0·76°	3·78°	7·44°	10·99°	14·42°	17·77°	
Boiling-point .	100·21°	101·10°	102·38°	103·99°	105·46°	107·27°	108·83

For more extended tables see *Chemical Technology*, vol. i. part 5.

Chloride of sodium is precipitated from its aqueous solution by passing hydrochloric acid into the liquid till it is saturated; this reaction is recommended by Margueritte for separating the salt from brine-liquors. Chloride of sodium is insoluble in pure alcohol, but is taken up in considerable quantity by dilute spirit.

Chloride of sodium unites with other metallic chlorides, forming crystallisable double salts; these are described with the chlorides of the several metals.

SODIUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions.*—Sodium-compounds impart an intense yellow colour to the outer blowpipe-flame, which quite conceals the coloration produced by any other metal. Alcoholic solutions of sodium-salts burn with a yellow flame. The spectrum of sodium is distinguished by a single bright-yellow line, coinciding with the dark solar line D.

2. *Reactions in Solution.*—Sodium-salts are even more generally soluble than potassium-salts. They give no precipitate with *platinum-chloride, tartaric acid*, or *perchloric acid*, and no crystals of alum with *sulphate of aluminium*. *Silicofluoric acid* gives a gelatinous precipitate in concentrated solutions.

Acid metantimonate of potassium (i. 326) gives a white precipitate of metantimonate of sodium, flocculent at first if the solution is not very dilute, but soon becoming crystalline. It is produced immediately, in solutions containing not less than 1 pt. of sodium-salt in 300 pts. of liquid. In more dilute solutions the precipitation is gradual, and the metantimonate of sodium is deposited in crystals on the sides of the vessel, the effect being apparent after 12 hours, even in solutions containing not more than $\frac{1}{1000}$ pt. of sodium-salt. The solution of sodium to be tested should be neutral or slightly alkaline, for free acid would separate antimonic acid from the reagent. It must also be free from salts of lithium, ammonium, and the earth-metals, all of which, when diluted to a certain extent, yield precipitates of similar character.

3. *Estimation and Separation.*—Sodium is estimated as sulphate or chloride, in the manner already described for potassium (iv. 699).

Sodium is separated from all the metals of Groups i. and ii. (Analysis, i. 217), by sulphydric acid and sulphide of ammonium; from the alkaline earth-metals by carbonate of ammonium; from magnesium by baryta-water; from potassium by platinic chloride and alcohol; from lithium by the solubility of lithium-chloride in alcohol and ether.

The separation of sodium from potassium is best effected when the metals are in the form of chlorides. The amount of potassium being determined from the weight of the chloroplatinate, that of sodium may frequently be estimated by difference. To estimate the sodium directly, the filtrate from the potassium-salt must be evaporated to dryness at a very gentle heat, and the residue ignited in a platinum crucible till the sodic chloroplatinate and the excess of platinic chloride are entirely decomposed; this decomposition is facilitated by adding a few crystals of oxalic acid during the ignition. The chloride of sodium thus formed is dissolved out by water, evaporated to dryness, ignited, and weighed. Removing the platinum by sulphydric acid does not give good results (H. Rose). The indirect method of analysis (i. 224) may also be advantageously applied, in many cases, to the estimation of potassium and sodium when they occur together.

4. *Atomic Weight of Sodium.*—Berzelius found that 100 pts. of sodium-chloride, NaCl, gave by precipitation 244·6 pts. silver-chloride; the atomic weight of sodium thence deduced is 23·17. Penny (Phil. Trans. 1839, p. 13), by determining the quantity of sodic nitrate produced by decomposing a given weight of sodic chloride with nitric acid, obtained, as a mean of seven closely-agreeing experiments, Na = 23·0. Pelouze (Ann. Ch. Pharm. lvi. 202) found, as a mean of three experiments, that 100 pts. of silver required for precipitation 54·144 pts. sodium-chloride: whence Na = 22·97. Dumas (*ibid.* cxiii. 31), as a mean of seven experiments of a similar kind, found Na = 23·01; and Stas found Na = 23·05. The atomic weight of sodium may therefore be taken as 23.

SODIUM, FLUORIDE OF. NaF. Obtained by saturating hydrofluoric acid with carbonate of sodium. It crystallises in white anhydrous cubes or octahedrons, soluble in 25 pts. of cold, and not much more soluble in hot water; the solution attacks glass. The fluoride is insoluble in alcohol.

Sodio-hydric fluoride, NaF.HF, crystallises by spontaneous evaporation from a solution of sodic fluoride supersaturated with hydrofluoric acid, in small rhombohedrons, having the angle of the terminal edges = 74° 36′, and often united in twins, having oP for the face of junction. (Marignac, Jahresb. 1857, p. 128.)

A *sulphato-fluoride of sodium*, $NaF.Na^2SO^4$, was found by Marignac (*ibid.* 1859, p. 106) to separate from the mother-liquor obtained in the preparation of sodium-fluoride with hydrofluoric acid containing a little sulphuric acid, in small hexagonal plates, which could be recrystallised from water without decomposition.

Fluoride of Sodium and Aluminium. Cryolite, $3NaF.AlF^3$ (i. 159).—This mineral is now used for the preparation of soda.

SODIUM, HYDRATE OF. $NaHO$ or $Na^2O.H^2O$. *Caustic Soda, Hydrated Oxide of Sodium, Mineral Alkali, Natronhydrat.*—This compound is formed when the protoxide or the dioxide of sodium is brought in contact with water, the action being attended with rise of temperature, and, in the latter case, with evolution of oxygen. It is prepared, like caustic potash, by decomposing sodic carbonate with lime; 3 pts. of crystallised sodic carbonate are dissolved in 15 pts. of boiling water, and a quantity of cream of lime, prepared by slaking 1 pt. of lime with 3 pts. of water, is added by small portions, the whole being boiled for some time, and treated as for potash (iv. 700). The hydrate thus obtained may be purified by alcohol. To obtain pure caustic soda without the use of alcohol, Gräger (J. pr. Chem. xcvi. 165) treats the carbonate, previously purified so far as to retain only a trace of chloride, with carbonate of silver, then boils it with calcined marble, and, lastly, filters the solution through a funnel, the throat of which is stopped with lumps of marble and pulverised marble, previously washed with distilled water.

In preparing caustic soda from the carbonate on the large scale, it is of importance to recover all the soda which remains diffused through the lime-mud. In some manufactories the mud is washed repeatedly, and the weak liquors are used either for dissolving fresh portions of carbonate, or for diluting the black ash-liquor; in other works the lime-mud is filtered in the following manner:—A shallow tank of stone or flags is so built that the bottom inclines towards one part, from which a pipe leads away the filtrate: rows of porous firebricks are set lengthways, three inches apart in the bottom of the tank, and upon these are laid in cement porous quarls, which form the filtering-bed. The lime-mud is run on to this bed and allowed to filter for some time, after which a few inches of water are gently run on to the pasty mass, so as not to disturb the particles. When this is properly managed, the water forces a strong ley out of the precipitate, without much diminution of its strength. The filtering-bed may also be constructed of large stones, gravel, and fine sand.

Caustic soda is now made in large quantity from black ash-liquors. For this purpose the liquors are concentrated in a fishing or boat-pan 30 feet long, 8 feet wide, and 2½ feet deep at the greatest depth, up to a specific gravity of 1·40, at a temperature of 260° or 270° F., whilst a little nitrate of sodium is added to oxidise the sulphate of sodium in the black ash. The separating salts are fished out, and the liquor is run into settlers, where more salts deposit during the cooling. The liquor is now run into a hemispherical cast-iron pot (about 5 feet diameter at the top, and 5½ feet deep, including a cast-iron ring about 2½ feet high), and more nitrate of sodium is added. It is boiled in this pot from 12 to 24 hours, during which a further deposit of salts takes place, which are fished out. The liquor is then transferred into another similar pot, called the "finisher," and boiled until it contains 60 per cent. of soda, during which more nitrate of sodium is added, while a thick scum which forms on the surface is skimmed off. When the concentration is complete, the fire is withdrawn, and the melted mass allowed to settle, after which it is run off into iron casks, or on to plates, to solidify.

Arrott proposes to produce a caustic soda from sulphide of sodium, with the aid of the oxides of iron or manganese. Hunt recommends the boiling of the solution of sulphide of sodium with oxide of zinc or black oxide of copper. Gossage has patented the manufacture of caustic soda from silicate of sodium by decomposition with lime, and proposes to employ the resulting calcic silicate as manure. Any of the other methods described for the preparation of caustic potash may also be applied to soda. F. O. Ward proposes to prepare it from albite, in the same manner as potash from orthoclase, by calcining the mineral with lime and fluor-spar. According to another method, patented by Newton, felspar is heated with calcic phosphate and lime, all in powder, at a low red heat, whereby calcic silicate and alkaline phosphate are produced; and when the mass is lixiviated with water, the lime decomposes the alkaline phosphate, reproducing calcic phosphate, while the alkali remains in solution.

Cryolite is now employed as a source of soda on the manufacturing scale in several places on the Continent (Copenhagen, Harburg, &c); the old process was to treat the finely-ground cryolite with sulphuric acid, but this plan is now entirely abandoned. The cryolite is ground to powder and mixed with lime, and either calcined or boiled with as much water as will form a milk. The boiling must be continued for several hours. When the mixture has been calcined, the mass must be exhausted with water. The hydrofluoric acid, alumina, and lime form an insoluble compound, while the caustic soda remains in solution. The following equation shows the change:—

$$AlF^3.3NaF + 3Ca''H^2O^2 = 3NaHO + Al'''H^3O^3 + 3Ca''F^2.$$

Hydrate of sodium is a white, opaque, brittle substance, having a fibrous texture, and specific gravity = 2·00 (Dalton). It melts below redness, but is less volatile at a red heat than hydrate of potassium. It colours the blowpipe-flame intensely yellow.

Crystallised Sodic Hydrate.—Soda-ley of specific gravity 1·385, cooled to 0°, yields large glassy crystals of a hydrate containing $2NaHO.7H^2O$, or $Na^2O.8H^2O$. It melts at 6°, forming a liquid of specific gravity 1·405; absorbs carbonic acid rapidly from the air, water more slowly; gives off half its water in a vacuum over oil of vitriol. It crystallises also very pure from a solution of caustic soda containing sulphate or chloride of sodium (Hermes, Pogg. Ann. cxix. 170). According to G. Rose (Jahresb. 1863, p. 179), the crystals are monoclinic, exhibiting the combination $oP \,.\, \infty P \,.\, +P \,.\, -P \,.\, +2P\infty \,.\, [\infty P\infty]$; tabular by predominance of oP. Angle $\infty P : \infty P$ (clinod.) = 98°; oP: the clinodiagonal prismatic edge = 104°; $2P\infty$: the same = 137°; $oP : \infty P$ = 98° (approximately).

Soda-ley.—Prepared as above from the carbonate, or by dissolving the solid hydrate or anhydrous sodic oxide in water. It is a colourless caustic liquid. A saturated solution at common temperatures has a specific gravity of 1·500 (Dalton); boils at 130°, and contains 36·8 per cent. of soda. 100 pts. of water dissolve, at 18°, 60·53 pts. of hydrate, or 41·43 pts. of dry soda; at 32°, 72·91 hydrate or 45·72 dry soda; at 55°, 100 hydrate or 63·53 dry soda; at 70°, 116·75 hydrate or 71·98 dry soda; and at 80°, 127·02 hydrate or 78·3 dry soda (Osann):—

Amount of Anhydrous Soda (Na^2O) *in a Solution of Caustic Soda, according to* Tünnermann.

Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.	Specific gravity.	Per cent.
1·4285	30·220	1·3198	22·363	1·2392	15·110	1·1042	7·253
1·4193	29·616	1·3143	21·894	1·2280	14·50	1·0948	6·648
1·4101	29·011	1·3125	21·758	1·2178	13·901	1·0855	6·044
1·4011	28·407	1·3053	21·154	1·2058	13·297	1·0764	5·440
1·3923	27·802	1·2982	20·550	1·1948	12·692	1·0675	4·835
1·3836	27·200	1·2912	19·945	1·1841	12·088	1·0587	4·231
1·3751	26·594	1·2843	19·341	1·1734	11·484	1·0500	3·626
1·3668	25·989	1·2775	18·730	1·1630	10·879	1·0414	3·022
1·3586	25·385	1·2708	18·132	1·1528	10·275	1·0330	2·418
1·3505	24·780	1·2642	17·528	1·1428	9·670	1·0246	1·813
1·3426	24·176	1·2578	16·923	1·1330	9·066	1·0163	1·209
1·3349	23·572	1·2515	16·379	1·1233	8·462	1·0081	0·604
1·3273	22·967	1·2453	15·714	1·1137	7·857	1·0040	0·302

(See also Richter's Tables, *Stöchiometrie*, iii. 332; Dalton's Elements, ii. 315).

The reactions of caustic soda are the same as those of potash, excepting that it gives no precipitate with platinic chloride, tartaric acid, or perchloric acid. It is very extensively used for making soap, and indeed for all purposes for which a caustic alkali is required, as it is cheaper than potash, weight for weight, and, moreover, as its combining number is less, a smaller quantity suffices to do a given amount of work.

SODIUM, IODIDE OF. NaI.—This salt is contained in the mother-liquors of kelp. It may be prepared by dissolving iodine in a strong solution of soda, evaporating, and slightly calcining the residue to decompose the iodate formed at the same time. It crystallises from aqueous solution, at 20° and upwards, in anhydrous cubes; at lower temperatures in hexagonal plates containing $NaI.2H^2O$. The anhydrous salt melts when heated, and volatilises at a higher temperature, giving off part of its iodine. It is deliquescent, easily soluble in water and in alcohol; 100 pts. water at 14° dissolve 173 pts. of it. The following relations between the specific gravity and strength of the aqueous solution have been determined by Kremers (Jahresb. 1858, p. 40), the specific gravities being referred to water at 19·5° as unity:—

Quantity of NaI in 100 parts of water	24·5	50·2	79·4	115·6	149·7
Specific gravity of solution	1·1752	1·3362	1·4962	1·6659	1·8047

The following table exhibits the expansion of solutions of sodium-iodide at different temperatures (Kremers, Jahresb. 1859, p. 49):—

Volumes of Aqueous Sodium-Iodide at different temperatures (vol. at 19·5° = 1).

Quantity of Salt in 100 pts. of Water.	31·8	64·5	99·9	138·0
Specific gravity at 19·5°	1·2234	1·4155	1·5942	1·7603
0°	0·99272	0·09030	0·98934	0·98918
19·5	1·00000	1·00000	1·00000	1·00000
40	1·00942	1·01104	1·01169	1·01179
60	1·02021	1·02264	1·02366	1·02382
80	1·03257	1·03514	1·03614	1·03621
100	1·04612	1·04840	1·04917	1·04887

A saturated aqueous solution of sodium-iodide boils at 141° (Kremers).

A compound of *sodic iodide* and *iodate*, $3NaI.2NaIO^3.20H^2O$, crystallises in hexagonal tables, oR . ∞R with + R, $-\frac{1}{2}$ R, &c. Angle, oR : + R = 115° 7′; oR : $-\frac{1}{2}$ R = 133° 10′. (Marignac, Jahresb. 1857, p. 124.)

SODIUM, OXIDES OF. Sodium forms a protoxide and a dioxide.

The *protoxide*, Na^2O, or *anhydrous soda*, is produced, together with the dioxide, when sodium burns in the air, and may be obtained pure by exposing the dioxide to a very high temperature, or by heating sodic hydrate with an equivalent quantity of sodium: $NaHO + Na = Na^2O + H$. It is a grey mass, having a conchoïdal fracture, melts at a red heat, volatilises with difficulty, is a non-conductor of electricity. Specific gravity = 2·805 (Karsten).

Dioxide or *Peroxide of Sodium*, Na^2O^2, is obtained by igniting sodium in oxygen-gas till its weight becomes constant. It is of a pure white colour, but becomes yellow when heated, and white again on cooling. When exposed to the air, it slowly deliquesces, and after a while resolidifies as carbonate. On mixing it with water, great heat is produced, and a small quantity of gas is evolved (arising from the local heating of the peroxide). A small heap of it, when moistened, becomes yellow with heat, and gives off a considerable quantity of oxygen. If, on the contrary, it be thrown into water in the state of powder by small portions at a time, it dissolves with very little evolution of gas, and forms a solution of dioxide.

A solution of the dioxide evaporated over a water-bath, gives off oxygen slowly at first, but rapidly as the solid residue begins to separate; but if evaporated slowly over oil of vitriol at common temperatures, it yields, without evolution of oxygen, large hexagonal tabular crystals of a hydrate, containing $Na^2O^2.8H^2O$.

These crystals, when left to effloresce over oil of vitriol for nine days, lost three-fourths of their water, and yielded another hydrate containing $Na^2O^2.2H^2O$.

Iodine decomposes sodic dioxide, forming an oxyiodide and liberating oxygen:

$$Na^2O^2 + I^2 = Na^2I^2O + O.$$

The dioxide absorbs *carbonic oxide*, forming sodic carbonate:

$$Na^2O^2 + CO = Na^2CO^3.$$

With *carbonic anhydride*, the same compound is formed, and 1 at. oxygen set free. With *nitric oxide* it forms sodic nitrite:

$$Na^2O^2 + 2NO = 2NaNO^2.$$

With *nitrous oxide* the same salt is formed, and 2 at. nitrogen given off:

$$Na^2O^2 + 2N^2O = 2NaNO^2 + N^2.$$

(A. Vernon Harcourt, Chem. Soc. J. xv. 267.)

SODIUM, OXYIODIDE OF. Na^2I^2O, or $NaI.NaIO$?—Produced, as above mentioned, by the action of iodine on sodic dioxide. It dissolves in acidulated water with separation of iodine:

$$Na^2I^2O + HCl = NaHO + NaCl + I^2.$$

SODIUM, SULPHIDES OF. Sodium forms with sulphur a number of compounds corresponding exactly with the sulphides of potassium (iv. 707), and prepared in the same manner. The protosulphide, Na^2S, crystallises in large octahedrons, and forms a large number of sulphosalts, most of which are crystallisable. Hydrate and carbonate of sodium react with sulphur, both in the wet and in the dry way, in the same manner as hydrate and carbonate of potassium.

SODIUM, TELLURIDE OF. Analogous to telluride of potassium.

SOILS. The term "soil" is applied to the upper stratum of the earth's crust,—that which is available for the growth of plants. A soil consists of mineral substances resulting from the decomposition or weathering of rocks, mixed with organic matter—the so-called *humous substances*—produced by the decay or putrefaction of plants which have grown upon it, and in cultivated soils, with the various substances, organic and inorganic, added in the form of manure. The stratum immediately below the cultivable soil, consisting of disintegrated rock, not touched by the spade or plough, and reached only by the deeper-rooting plants, is called the "subsoil."

The soil is the source whence plants derive the whole of their mineral food. All plants require for their nutrition phosphoric acid, sulphuric acid, alkalis, lime, magnesia, and iron: many species require silica; those which grow on the seashore require sodium-salts and metallic iodides. All the compounds required for the nutrition of plants are, in a certain sense, of equal value: if one of them is wanting in the soil, or present only in a form which cannot be taken up by the roots, the plant will not flourish.

The organic constituents of the soil serve as sources of carbonic acid and ammonia. The ammonia is produced by the putrefaction of nitrogenous matters—the carbonic acid by the oxidating action of air penetrating the soil on the carbon of the humous substances. The carbonic acid thus produced not only serves as a source of carbon to the growing plant, but likewise assists in the disintegration of the mineral constituents of the soil, by dissolving the earthy phosphates and decomposing the felspathic minerals. Chloride and nitrate of sodium and ammoniacal salts likewise dissolve the phosphates of calcium and magnesium, and thus contribute to diffuse them through the soil.

It was formerly supposed that the constituents of a soil could not be taken up by the roots of plants, unless they were in the state of solution; but later researches have shown that this is not the case, but that soils, especially those which contain abundance of decayed vegetable matter or humus, have the power of absorbing the acids, alkalis, and salts which filter through them in the state of solution, and retaining these substances in a state of loose combination, in which they are ready to be taken up by the roots of plants.

In 1845 H. S. Thomson (Agr. Soc. J. xi. 68) observed that when solutions of sulphate or carbonate of ammonium are filtered through soils, the first portions of the filtrate contain only traces of ammonia, but, in the case of the sulphate, a considerable quantity of gypsum. Huxtable, about the same time, found that dunghill water filtered through a loamy soil loses its colour and odour.

These observations were further extended by Way (Agr. Soc. J. xi. 313), who showed that certain constituents of farmyard manure, when brought in contact, in the state of solution, with arable soil, lose their solubility, and unite in a peculiar manner with the soil. Caustic ammonia, and sulphate, nitrate, and chloride of ammonium, treated in aqueous solution, with excess of soil, give up their ammonia to it completely; while the sulphuric, nitric, or hydrochloric acid unites with other bases (generally lime) contained in the soil, forming soluble salts which filter through. A similar absorptive power is exerted by the particles of a soil on potash, whether in the caustic state, or in the form of potassic sulphate, nitrate, or chloride. Solutions of sodium and magnesium-salts likewise give up their bases to the soil. Phosphates, however, are not affected by the soil in the same manner as sulphates, nitrates, and chlorides, inasmuch as from solutions of sodic phosphate, or from a solution of guano-ash in dilute sulphuric acid, the phosphoric acid, as well as the base, is withdrawn by the particles of the soil. Way likewise found that putrid urine, the retting water of flax, and sewage-water, are deprived by contact with soil, of their ammonia, potash, and phosphoric acid.

The absorptive power of a soil for potash, ammonia, and phosphoric acid can scarcely be regarded as a definite chemical action, inasmuch as it is exerted in an equal degree by soils of the most various composition: a soil abounding in clay, with a small proportion of lime, possesses it in the same degree as a lime-soil containing a small free portion of clay; it is, however, considerably affected by the quantity of humus present in the soil.

The absorptive power of arable soil depends very much on its degree of porosity; a dense heavy clay-soil and a loose sandy soil possess it in the least degree, and it is most strongly exhibited by those soils which have a light porous structure, like wood or charcoal; in fact, it is similar to the surface-attraction exerted by charcoal on colouring-matters, the attracted particles not entering into a new chemical combination, but retaining their original properties. When a salt, such as sulphate of ammonium or potassium, gives up its base to the soil, the acid separated therefrom enters into combination with lime or magnesia contained in the soil. The attractive force of the earthy particles for the alkali would probably not be sufficient in itself to separate it from the sulphuric or nitric acid, but the decomposition takes place when assisted by the additional attraction of the lime or magnesia for the sulphuric or nitric acid.

Absorption of nutriment from the soil is effected by the extremities of the roots, which must therefore be in immediate contact with the nutritive particles, and hence the necessity of sufficient porosity in the soil to enable the roots to spread and ramify in all directions through it. "The effect produced by breaking up the ground with the plough, spade, hoe, harrow, and roller, depends upon the fact that the roots of plants go in search of their food, that the nutritive substances have no locomotion of their own, and cannot of themselves leave the places in which they are. The root, as if it had eyes to see, bends and stretches in the direction of the nutriment; so that the number, thickness, and direction of its filaments indicate the precise spots where they have obtained food." (Liebig, *The Natural Laws of Husbandry*, London 1853, chapter ii.)

Analysis of Soils.*—The method at present adopted for the analysis of soils is essentially the same as that described by Sprengel and Otto in Sprengel's "Bodenkunde;" depending on the principle, that in order to judge of the fertility of a soil, it is necessary to determine not only what are its elementary constituents, but likewise the manner in which they are combined. With this view, Sprengel and Otto treated a sample of the soil successively with water, dilute hydrochloric acid, strong sulphuric acid, and by fusion with an alkaline carbonate. The constituents of the soil soluble in water were supposed to be actually available as plant-food; those which were soluble in dilute acids as available for that purpose after being subjected to the action of carbonic acid and the humous acids of the soil; the rest as available only after the soil had been subjected for a considerable time to atmospheric influences, assisted by the mechanical operations of tillage. This mode of proceeding was originally based upon the supposition that the constituents of the soil which are to nourish the plant must be presented to it in the state of solution, a view which, as already observed, can no longer be regarded as correct. Still, as the several constituents must be brought into the state of solution before they can be distributed through the soil, and be taken up by its particles in the state of physical aggregation above described, the separation of the soil into portions soluble in water and acids, and an insoluble portion, is still capable of affording useful information as to its nutritive properties.

a. Constituents soluble in Water.—An average sample of the soil having been obtained, and freed from stones and the coarsest particles by sifting, the original plan was to heat a considerable quantity of it (1000 to 2000 grms.) with water nearly to the boiling-point, then filter; wash the residue as completely as possible with hot water; evaporate the entire liquid to about the volume of the water first employed; filter again to separate any deposit that may have formed; then determine the volume of the filtrate; and employ measured quantities of it for estimating the several constituents.

The total amount of the constituents soluble in water is obtained by evaporating a measured quantity of the solution to dryness, and weighing the residue when it no longer loses weight at 100°. The dry residue is then gently ignited for some time in contact with the air, and weighed after drying over oil of vitriol, the loss of weight thus determined being reckoned as organic matter, nitric acid, and ammonia, supposing the presence of the two latter substances to have been previously ascertained by qualitative analysis. The ignited residue is then treated with hydrochloric acid, and evaporated to dryness; the remaining substance is exhausted with dilute hydrochloric acid, and the undissolved silica separated by filtration.

The filtrate is next treated with chlorine-water, and ammonia is added, whereby a precipitate is formed containing alumina, ferric oxide, manganic oxide, and phosphoric acid, together with a portion of the lime and magnesia, in case the quantity of phosphoric acid is considerable. This precipitate is collected and weighed, and its several constituents are separated and estimated in the manner already described with reference to the ash of organic bodies (i. 419). If its quantity is too small for the estimation of all the constituents, the phosphoric acid should at least be determined.

The filtrate from the last-mentioned precipitate is mixed with oxalate of ammonium to separate lime. If this base is present, the solution cannot contain any more phosphoric acid; it is then to be filtered and evaporated, the residue ignited to expel ammoniacal salts, then dissolved in water, and treated by the usual methods for separating the **magnesia, potash,** and **soda.** If, on the other hand, the alkaline earths have been wholly precipitated, together with phosphoric acid, in the liquid filtered from the silica, phosphoric acid may still be present in the filtrate containing the alkalis. In that case the phosphoric acid may be separated by methods already described (iv. 549).

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* Sprengel's *Bodenkunde*, 1837, p. 370.—Fresenius, *Anleitung zur quantitativen Analyse*, 4. Aufl. p. 518.—Wöhler, *Uebungen in der Analyse*, 1853, p. 167.—E. Wolff, *Anleitung zur Untersuchung landwirthsch. wichtiger Stoffe*, 1857, p. 71.—Fraas, *Die Natur der Landwirthschaft*, 1857. i. 125.—W. Mayer, *Ergebnisse landwirthsch. u. agricultur-chemische Versuche*, München, Heft i. S. 127.—Boussingault, *Compt. rend.* xlvi. 1126.—H. Rose, *Chimie Analytique*, ii. 931.—*Handb. d. Chem.*, 2te Aufl. ii, [2] 246.

Separate quantities of the aqueous extract of the soil are used for estimating **sulphuric acid** by chloride of barium, and **chlorine** by nitrate of silver. **Carbonic acid,** if present, is estimated in a portion of the extract evaporated to a small bulk, by the method given under ALKALIMETRY (i. 119).

It is evident, however, that an aqueous extract prepared as above, by boiling with distilled water, cannot afford an exact representation of that solution which is actually formed in the soil by rain-water, under the varying atmospheric conditions to which the soil is exposed in the course of a season. To obtain such a solution, an instrument called a "lysimeter" is employed, consisting of a square box, usually made of zinc, open at top, closed at bottom, and having an internal area of exactly one square foot. At the depth of six inches from the upper edge is placed a perforated bottom; the space above this is filled with earth, and the box is sunk in the ground to the level of the upper edge. All rain-water which falls on this square foot of surface must, therefore, either evaporate or filter through the six-inch layer of soil and collect in the box below. The instrument is taken up and emptied every three months, or oftener if the amount of rain is greater than usual.

The following table contains the results of several analyses by Zöller of drainage-water collected in the lysimeter:—1. From manured lime-soil with vegetation.—2. Rough clay-soil with vegetation.—3. Rough clay-soil without vegetation.—4. Manured clay-soil without vegetation.—5. Manured clay-soil with vegetation:—

Lysimeter Waters, according to Zöller.

A million parts of water contain:	1	2	3	4	5
Solid residue at 100° .	472·32	254·64	292·64	305·20	291·50
Ash therein . .	317·62	176·74	194·78	214·50	212·16
Potash . . .	6·50	2·37	2·03	5·46	3·82
Soda	7·11	5·60	7·43	23·74	6·02
Lime	145·86	57·60	70·80	68·41	92·34
Magnesia . . .	20·52	8·80	1·32	2·93	5·12
Ferric oxide . .	1·32	6·35	8·26	5·76	4·30
Chlorine . . .	57·49	9·52	20·87	39·46	35·27
Phosphoric anhydride	2·23				
Sulphuric "	17·47	27·13	27·82	29·30	33·49
Silicic "	10·46	11·35	17·46	9·50	9·34

β. *Estimation of the constituents soluble in dilute Hydrochloric Acid.*—This is the most important part of a soil-analysis, inasmuch as it shows the total amount of those constituents of the soil which are readily available as plant-food. It was formerly made on the residue left after exhausting the soil with boiling water; but as this mode of extraction is no longer regarded as of much importance, it is now more generally made upon the soil in its original state, after mechanical separation of the stones and coarser particles.

A quantity of the soil (50 to 100 grms.) is mixed with water to a thin paste in a flask, and hydrochloric acid is gradually added, as long as any effervescence is thereby produced; the whole is then warmed for a time, with frequent agitation, then filtered, and the insoluble residue thoroughly washed. The filtered solution is evaporated to dryness, after addition of a little nitric acid; the silica is separated by filtration and weighed; and the filtrate is divided into several portions, which are measured or weighed, and used for the estimation (1) of **sulphuric acid**; (2), of **phosphoric acid, alumina, ferric oxide, manganous oxide, lime,** and **magnesia**; (3), of the **alkalis.** A separate portion serves for the estimation of **carbonic acid,** and another for that of **ferrous oxide,** supposing this oxide to be present in the soil together with ferric oxide. For this latter purpose, Fresenius adopts Margueritte's method with potassic permanganate (i. 263; iv. 384), which, however, is not applicable when organic matter is present. In this case it is best to digest the soil with hydrochloric acid in an atmosphere of carbonic anhydride, then nearly neutralise the free acid with sodium-carbonate, and add levigated barium-carbonate in excess, which will throw down the whole of the ferric oxide, leaving the ferrous oxide in solution. The liquid is then filtered in an atmosphere of carbonic anhydride; and the iron in the filtrate is brought to the state of ferric oxide by chlorine-water or nitric acid, and precipitated in that form by ammonia.

γ. *Portion insoluble in dilute Hydrochloric Acid.*—This portion of the soil generally consists of clay and sand, mixed with other minerals. By heating a portion of it (5 to 10 grms.) with several times its weight of strong sulphuric acid, till the greater part of that acid is volatilised, the clay is decomposed, the other constituents remaining for the most part unaltered. The whole is left to cool, the nearly dry residue is treated with dilute hydrochloric acid, and the bases are determined in the filtered solution in the way already indicated (β). From the undissolved residue, the pulverulent silica separated from the clay may be dissolved out, though with considerable difficulty, by repeated boiling with strong solutions of sodic carbonate. There then remains a mixture of sand and other minerals not decomposible by oil of vitriol, the nature of which may generally be determined with sufficient accuracy by the microscope.

δ. *Estimation of Organic Matter.*—The total quantity of organic matter in a soil, consisting of remains of plants and products of decay (the so-called humous substances), may be roughly estimated from the loss of weight which the dried soil undergoes when exposed to a low red heat not strong enough to decompose the earthy carbonates. Many soils, however, especially those containing clay, give up a certain portion of water only at a red heat; moreover, ammonia and nitric acid may be included in the loss of weight obtained on ignition. Hence it is better to determine the amount of carbon in the soil by combustion with oxide of copper, deducting from the amount of carbonic anhydride thus obtained that which exists in the soil in the form of carbonates, or making the combustion on a portion previously freed from carbonates by treatment with dilute acid. Another method is to digest 5 grms. of the soil with 10 c. c. water and 15 c. c. oil of vitriol, allow the disengaged carbonic anhydride to escape, then add 5 grms. of acid potassic chromate, heat the liquid, and collect the carbonic anhydride thereby evolved. (Wolff.)

ε. *Estimation of Nitrogen.*—The entire quantity of nitrogen existing in a soil, in the form of ammonia, of nitric acid, and of organic compounds, may be estimated by combustion with oxide of copper, as in Dumas's method (i. 242). To determine the nitric acid, Wolff exhausts 500 grms. of the soil with cold water; evaporates the filtrate to 30 c. c.; mixes it with a little potash-ley, and boils till ammonia is no longer evolved; then reduces the nitric acid in the residual solution with zinc; and estimates it in the form of ammonia (iv. 88, 89).

No exact method has yet been discovered of determining the quantity of ammonia existing in a soil. W. Mayer found that even when ammonia was added to a soil, it could not be recovered with certainty by boiling with soda-ley.

The following tables exhibit the proportions of carbon and nitrogen found in several soils:—

Sandy soils of Saxony (Ritthausen).			Scotch wheat-soils (Anderson).				
				Upper soil.		Subsoil.	
	Carbon per cent.	Nitrogen per cent.		Carbon per cent.	Nitrogen per cent.	Carbon per cent.	Nitrogen per cent.
1	1·415	0·107	Mid-Lothian .	4·510	0·220	1·306	0·973
2	1·148	0·115	East Lothian .	1·981	0·130	1·563	0·150
3	1·537	0·126	Perthshire . .	2·550	0·210	2·030	0·170
4	2·163	0·113	Morayshire .	0·714	0·074	0·390	0·048
5	1·390	0·089					

Russian Black Earth from the Government of Tambow (Petzoldt).
In 100 *pts. of Earth dried at* 115°—120°.

	Loss by ignition.	Nitrogen.
Manured arable soil	18·18	0·17
Unmanured subsoil	9·48	0·33
Unmanured arable soil	8·28	0·30

SOIMONITE. Syn. with CORUNDUM.

SOLANICINE. $C^{50}H^{78}N^{2}O$ (?).—A base produced by the action of hydrochloric acid on solanine. A solution of solanine in cold concentrated hydrochloric acid assumes at first a reddish or violet, then a yellow colour, and afterwards yields a red-brown precipitate containing the hydrochlorates of two new bases sparingly soluble in alcohol. From the alcoholic solution of the precipitate, ammonia throws down a yellow gelatinous mass, which, after treatment with hot alcohol (to remove solanine and solanidine), is resolved, by repeated digestion with ether, into a base soluble with yellow colour, and another nearly insoluble in ether.

The soluble base appears to be impure solanidine. The other, solanicine, which dissolves only in 2,000 pts. of ether, and is very slightly soluble also in water and in alcohol, may be obtained by slow evaporation of its ethereal solution, in slender needles or crystalline flocks. It melts, with decomposition, above 250°; is coloured red by concentrated acids; and forms amorphous, yellow, nearly neutral salts, easily soluble in water and in alcohol, but insoluble in ether. The deep yellow solutions have an astringent bitter taste, and are precipitated by concentrated hydrochloric acid. The *hydrochlorate* has the composition $C^{50}H^{78}N^2O.2HCl$; the *chloroplatinate* is $C^{50}H^{78}N^2O.2HCl.Pt^{iv}Cl^4$. (Zwenger and Kind, Ann. Ch. Pharm. cxxiii. 341.)

Solanicine gives by analysis (mean) 83·01 per cent. C, 10·83 H, 3·87 N, and 2·29 O, agreeing nearly with the formula $C^{50}H^{78}N^2O$, which requires 83·10 C, 10·80 H, 3·88 N, and 2·22 O. If it contained 2 at. hydrogen more, or if solanidine contained 2 at. hydrogen less, it might be supposed to be formed from solanidine by abstraction of H^2O; but neither of these suppositions agrees well with the analytical results. The formulæ of solanine and all its derivatives require further investigation.

SOLANIDINE. $C^{25}H^{41}NO$ (?).—A base produced, together with glucose, by the action of acids on solanine. It was discovered about the same time by Zwenger and Kind (Ann. Ch. Pharm. cix. 244), and by O. Gmelin (*ibid.* cx. 167), the latter of whom regards it as non-nitrogenous (p. 346). It is best prepared by boiling solanine with dilute hydrochloric acid, washing the precipitated hydrochlorate of solanidine with water, recrystallising it from alcohol mixed with ether, precipitating the alcoholic solution by ammonia, and recrystallising the precipitated base, first from alcohol, then from ether. (Zwenger and Kind.)

Solanidine dissolves easily in alcohol and in ether, but is nearly insoluble in water. It crystallises from alcohol in long colourless silky needles, from ether in thicker crystals, exhibiting, when magnified, the form of four-sided prisms. The solutions have a bitter somewhat astringent taste (Zwenger and Kind). The alcoholic solution gives a yellowish-brown precipitate with iodine (Kromayer). When quickly heated it melts above 200°, and sublimes almost without decomposition; when slowly heated, it decomposes more easily. From the solutions of its salts it is precipitated by ammonia, or the fixed alkalis, in the amorphous state. It is not decomposed by boiling potash-ley, and does not reduce chloride of gold, nitrate of silver, or an alkaline cupric solution. With moderately strong sulphuric acid, it gradually forms a dark-red solution, containing two new bases precipitable by water. With more dilute sulphuric acid, especially on addition of alcohol, it exhibits (like solanine) a transient bluish-red colouring, by which small quantities of it may be recognised.

Zwenger and Kind found in solanidine (mean of three analyses), 80·92 per cent. carbon, 11·15 hydrogen, 3·79 nitrogen, and 4·10 oxygen. The formula $C^{25}H^{41}NO$ requires 80·87 carbon, 11·05 hydrogen, 3·77 nitrogen, and 4·31 oxygen.

Salts of Solanidine.—Solanidine has a somewhat stronger alkaline reaction than solanine, and forms both neutral and acid salts, mostly crystallisable, bitter, sparingly soluble in water and in acids.—The *hydrochlorate*, $C^{25}H^{41}NO.HCl$, deposited from the solution of the base in alcohol containing hydrochloric acid, and recrystallised by slow evaporation from alcohol, forms rhombic prisms with end-faces; slightly soluble in water and in hydrochloric acid, easily in alcohol, and volatilising without decomposition when heated.—The *chloroplatinate*, $2C^{25}H^{41}NO.2HCl.Pt^{iv}Cl^4$, separates in yellowish flocks, when a solution of solanidine in alcohol containing hydrochloric acid, is mixed with platinic chloride and poured into cold water.—The *nitrate*, prepared like the hydrochlorate, crystallises in tufts of needles.—The *sulphate* is easily soluble in alcohol, less easily in water, and separates partly in slender needles, partly as an amorphous powder, apparently a mixture of the neutral and acid sulphates. (Zwenger and Kind.)

SOLANINE. $C^{43}H^{71}NO^{16}$ (?).—An organic base discovered in 1820 by Desfosses (J. Pharm. vi. 374), in the berries of the black nightshade (*Solanum nigrum*), and subsequently obtained from several other species of solanum; *e. g.*, from the berries of *Solanum verbascifolium*, from the berries and (in small quantity) from the tubers and green parts of the potato (*S. tuberosum*), but especially in the flowers, stalks, and berries of the woody nightshade (*S. Dulcamara*), and in the shoots or germs which potatoes throw out when kept in cellars during winter (0·068 per cent. according to J. Wolff and Blanchet). Solanine has been investigated by Desfosses (*loc. cit.*), by Payen and Chevallier (J. chim. méd. i. 517), O. Henry (J. Pharm. xviii. 661; xx. 54), Otto (Ann. Ch. Pharm. vii. 150, xxvi. 232), and others, and more recently by

Moitissier (*ibid.* i. 368), **Zwenger** and **Kind** (*ibid.* cix. 244; cxviii. 129), and **O. Gmelin** (*ibid.* cx. 167). The results of these several investigations exhibit many points of difference, possibly because the crystallisable bases obtained from different species of solanum are not really identical, or because many of the products examined were impure.

Preparation.—1. From *Potato-shoots.*—The fresh shoots are boiled in water slightly acidulated with sulphuric acid; the rapidly expressed liquid is precipitated, while still warm, by ammonia; the dried precipitate is exhausted with boiling alcohol; and the solanine, which separates almost completely on cooling, is several times crystallised from alcohol, till it dissolves in hydrochloric acid without turbidity. Fresh rather short potato-shoots, not too much developed, yield the largest quantity (**Reuberg**, Ann. Ch. Pharm. xxx. 225.—**Zwenger** and **Kind**).—As solanine is easily resolved, by heating with acids, into solanidine and sugar, care must be taken not to use the acid too strong or in too large quantity. Acetic acid, which does not decompose solanine, would perhaps be better adapted for the preparation than sulphuric or hydrochloric acid. According to **Kromayer** (Arch. Pharm. [2], cxvi. 214; Jahresb. 1863, p. 450), solanine is most easily obtained by precipitating the expressed juice of the potato-germs with lime, without using acid, and exhausting the precipitate with alcohol.

2. From *Potato-tubers.*—The potatoes rubbed to a pulp are digested in water containing sulphuric acid; the filtrate is boiled to separate albumin; the liquid again filtered, and precipitated with milk of lime; and the precipitate treated with alcohol.

3. From the berries of *Solanum nigrum*, &c.—The ripe berries are pressed; the juice is precipitated by ammonia, and the grey pulverulent precipitate is purified by recrystallisation from alcohol, with aid of animal charcoal.—Peschier dissolves the impure precipitate in acetic acid, precipitates the filtrate with ammonia, and then treats it with boiling alcohol.—Payen and Chevallier exhausted the dried berries of *Solanum verbascifolium* with alcohol, treated the extract which remained on evaporation with water, and precipitated the aqueous solution with magnesia, whereby impure solanine was obtained.

Properties.—Solanine (from potato-shoots) is slightly soluble in cold, easily in hot alcohol, and crystallises therefrom in slender silky needles, which under the microscope present the appearance right-angled four-sided prisms. It is nearly insoluble in water and in ether. From its solution in acids, it is completely separated by alkalis as a white gelatinous precipitate. It has a slightly bitter and somewhat burning taste, and faint alkaline reaction. It is very poisonous, two or three grains being sufficient to kill a rabbit in a few hours,—first, however, producing paralysis of the hinder extremities. The same symptom has been observed in oxen after eating potato-shoots. It melts at about 235° to a yellowish liquid, solidifying to an amorphous mass. At a stronger heat, it emits the odour of burnt sugar (**Zwenger** and **Kind**). When a very small quantity of it, in the state of fine powder, is heated on a piece of platinum-foil having in the middle a hemispherical depression covered with a small watch-glass, it sublimes in a network of slender needles. (**Helwig**, Anal. Zeitschr. iii. 43.)

The analyses of solanine by different chemists exhibit great diversity, as the following table will show:—

	From Solanum Dulcamara.		*From Potato-shoots.*		
	Henry.	Moitissier.	Blanchet.	O. Gmelin.	Zwenger u. Kind.
Carbon . .	75·0	60·9	62·0	62·2	60·01
Hydrogen .	9·1	8·7	8·9	8·7	8·40
Nitrogen .	3·1	3·6	1·6		1·37
Oxygen .	12·8	26·8	27·5	29·1	30·22
	100·0	100·0	100·0	100·0	100·00

Henry's analysis, which differs widely from all the rest, may be represented by the formula $C^{112}H^{82}N^{2}O^{15}$; Blanchet's by $C^{90}H^{77}NO^{30}$ or $C^{45}H^{77}NO^{15}$. Moitissier deduces from his own analysis the formula $C^{42}H^{35}NO^{14}$ or $C^{21}H^{25}NO^{7}$. Zwenger and Kind's results may be represented by the formula $C^{43}H^{71}NO^{16}$, requiring 60·21 per cent. carbon, 8·28 hydrogen, 1·63 nitrogen, and 29·88 oxygen.* O. Gmelin found variable quantities of nitrogen in solanine, and is of opinion that the pure substance is free from nitrogen: he deduces from his analyses the formula $C^{44}H^{72}O^{15}$. But the basic character of solanine renders it most probable that it contains nitrogen.

Decompositions.—1. Solanine, subjected to dry distillation, yields solanidine together with acid empyreumatic products.—2. It is not decomposed by boiling *potash-ley*.—3. It reduces, when heated, a solution of *argentic nitrate* or *auric chloride*, but not an alkaline cupric solution.

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* [illegible] solanine the formula $C^{86}H^{70}NO^{32}$, for solanidine $C^{50}H^{40}NO^{2}$, and for two of which are inadmissible, because the sum of the hydrogen- and uneven. Moreover, they do not represent the numbers obtained by so closely as the formulæ $C^{43}H^{71}NO^{16}$ and $C^{25}H^{41}NO$.

4. Solanine, warmed or boiled with *dilute sulphuric* or *hydrochloric acid*, easily splits up into solanidine and glucose, the sulphate or hydrochlorate of solanidine separating in the crystalline form, while the sugar remains dissolved. The decomposition is likewise produced by oxalic, but not by acetic acid. According to Zwenger and Kind, the reaction is:

$$\underset{\text{Solanine.}}{C^{43}H^{71}NO^{16}} + 3H^2O = \underset{\text{Solanidine.}}{C^{25}H^{41}NO} + 3C^6H^{12}O^6.$$

According to O. Gmelin it is:

$$\underset{\text{Solanine.}}{C^{44}H^{72}O^{15}} + 3H^2O + O^2 = \underset{\text{Solanidine.}}{C^{26}H^{42}O^2} + 3C^6H^{12}O^6.$$

The absorption of oxygen here supposed is, however, contrary to the analogy of all reactions of this kind. W. Delffs (Chem. Centr. 1859, p. 800) remarks that Gmelin's analysis of solanine may represented by the formula $C^{20}H^{32}O^7$, and his analysis of solanidine (81·9 and 82·0 per cent. C, and 10·6 to 10·8 H), by the formula $C^{14}H^{20}O$, according to which the reaction would be:

$$C^{20}H^{32}O^7 = C^{14}H^{20}O + C^6H^{12}O^6.$$

If this formula were correct, solanine (or rather solanin) would be a glucoside homologous with æsculin, $C^{11}H^{14}O^7$, arbutin, $C^{12}H^{16}O^7$, salicin, $C^{13}H^{18}O^7$, senegin, $C^{14}H^{20}O^2$, and perhaps smilacin, $C^{21}H^{34}O^7$. But, as already observed, it is more probable that solanine and solanidine contain nitrogen.

5. A cold-prepared solution of solanine in more concentrated *sulphuric* or *hydrochloric acid*, deposits on standing a bulky yellowish precipitate containing the salts of solanicine and another base (p. 345), formed from solanidine by the action of the strong acid. (Zwenger and Kind.)

6. With strong *nitric acid*, solanine forms a colourless solution, which exhibits after a while a transient red colour, and ultimately deposits a brown resin. (Zwenger and Kind.)

7. Solanine quickly absorbs vapour of *iodine*, forming iodosolanine, which is brown, permanent in the air, and dissolves with brown colour in water. An aqueous solution of sulphate of solanine likewise assumes a dark-brown colour on addition of aqueous iodine. According to Kromayer, an alcoholic solution of solanine mixed with a large quantity of iodine-water, turns red-brown but remains clear, whereas a solution of solanidine similarly treated yields a yellow-brown precipitate.

8. According to Moitissier, solanine (from *Solanum Dulcamara*), heated in a sealed tube with *ethylic iodide*, yields hydriodate of ethylsolanine, from which the base [$C^{21}H^{34}(C^2H^5)NO^7$, according to Moitissier's formula of solanine] is separated by ammonia as a mass of interlaced microscopic needles soluble in alcohol. Its salts are easily soluble, gummy, and poisonous. In like manner *amylic iodide* converts solanine into amylsolanine, and ethylsolanine into ethyl-amylsolanine. According to O. Gmelin, on the other hand, solanine (from potato-shoots) does not form any substitution-compound with ethylic iodide, even when the two are heated together for a long time, the resulting resinous mass, when dissolved in water and treated with ammonia, yielding nothing but solanine. Moitissier found, in his ethylsolanine, 62·2 per cent. carbon and 8·8 hydrogen, which agrees exactly with Gmelin's analysis of solanine itself.

Salts of Solanine.—Solanine forms both acid and neutral salts, all of which are easily soluble in water. The neutral salts have a faint acid reaction, and bitter, strongly burning taste; they dissolve easily in alcohol, remaining as gelatinous masses on evaporation, and are nearly insoluble in ether. The dilute aqueous solutions of solanine-salts, excepting the acid sulphate, gradually decompose, more quickly when heated, and deposit solanine. (Baumann, Arch. Pharm. xxxiv. 23.—Zwenger and Kind.)

Acetate of solanine cannot be obtained in the solid state without decomposition (Zwenger and Kind).—The *chromate* crystallises in dark-yellow needles.—The *gallate* is a soluble amorphous mass.—The *gallotannate* crystallises in needles, slightly soluble in cold, easily in hot water. (Baumann.)

The *hydrochlorate*, $C^{43}H^{71}NO^{16}.HCl$, is obtained by dissolving the base in alcohol and hydrochloric acid, and repeated precipitation with ether, as a gelatinous precipitate, which dries up to a gummy mass. The alcoholic solution of this salt mixed with platinic chloride, and then with ether, deposits the *chloroplatinate*, $2C^{43}H^{71}NO^{16}.2HCl.Pt^{iv}Cl^4$, as a yellow flocculent precipitate, which may be purified by repeated solution in alcohol and precipitation with ether. It is soluble in hot water, still more soluble in alcohol. (Zwenger and Kind.)

The *hydroferrocyanate* is precipitated in white flocks on mixing a solution of any solanine-salt with ferrocyanide of potassium.—The *mellitate* is soluble in water, the neutral solution depositing solanine when evaporated.—The *mucate* crystallises in slender easily soluble needles. (Baumann, Arch. Pharm. xxxiii. 23.)

The *oxalate*, $2C^{43}H^{71}NO^{16}.C^2H^2O^4.H^2O$, is obtained by evaporating a solution of solanine in aqueous oxalic acid, in white crystalline crusts mixed with amorphous salt: its aqueous solution deposits solanine when boiled. It gives off its water at 100°. (Zwenger and Kind.)

The *phosphate* is obtained by precipitation as a white crystalline powder.—The *succinate* crystallises in easily soluble slender needles.

SOLANOLEIC and **SOLANOSTEARIC ACIDS.** See POTATO-FAT (iv. 723).

SOLANUM. The most important plant belonging to this genus is the potato (*Solanum tuberosum*, iv. 720).

Solanum Dulcamara.—The stalks of this plant, which are used in medicine under the name of bitter-sweet, or *Stipites Dulcamaræ*, contain picroglycion or dulcamarin (iv. 642), together with solanine and other substances.

Solanum Lycopersicon.—The leaves of this plant are said to contain an alkaloïd soluble in water. The deep red somewhat acid fruits, called love-apples or tomatoes, contain a free acid—malic acid according to former statements, citric acid according to Bertagnini (Jahresb. 1860, p. 562); probably also solanine, together with volatile oil, uncrystallisable sugar, &c. (See Enz, Jahresb. 1862, p. 514.)

Various other species of solanum, especially the fruits, are said to contain solanine together with malic acid (?): e.g., *S. mammosum*, *S. nigrum*, and *S. verbascifolium*.

SOLAR OIL. A name applied in commerce chiefly to the heavier portions of petroleum and shale-oil, the lighter portions being called *photogen*, *hydrocarbon*, *&c.* (See PARAFFIN, iv. 346.)

SOLFATARAS. Craters of extinct volcanos, which give indications of their former activity by still emitting vapours and gases of various kinds, sometimes depositing sulphur, sal-ammoniac, and other solid minerals, on the walls of cavities in the craters.

SOLFATARITE. The name given by Shepard (Sill. Am. J. xvi. 203) to soda-alum, on account of its occurrence in the solfatara near Naples.

SOLUTION. The liquefaction of a solid or gaseous body by contact with a liquid, the solid or gas being diffused uniformly through the liquid, and not separating when left at rest. The liquid, which thus takes up or absorbs a solid or gas, is called the solvent or menstruum; and the product of the action, as well as the action itself, is called a solution.

The product formed by the union of liquids one with the other is usually called a mixture, if the two liquids are capable of uniting in any proportions whatever, as is the case with water and alcohol, or alcohol and ether; and a solution, when each of the liquids is capable of taking up only a limited quantity of the other. When two such liquids are brought together in such proportion that neither can dissolve completely in the other, two layers are generally formed, each containing an excess of one of the liquids. Thus, when water and ether are mixed in equal volumes, two layers are formed after a while, the upper consisting of ether holding water in solution, the lower of a solution of ether in water.

The solution of gases in liquids has already been considered under GASES, ABSORPTION OF, ii. 790; the present article relates to the solution of solids.

Respecting the difference between solution and definite chemical combination, see CHEMICAL AFFINITY (i. 851).

The solution of a solid in a liquid is usually attended with a fall of temperature, arising from the conversion of sensible into latent heat, which always accompanies the passage of a body from the solid to the liquid state (HEAT, iii. 79). In some cases, however, the actual solution of a solid is preceded by the formation of a definite chemical compound, and is then attended with rise of temperature: thus, anhydrous baryta or lime, and many anhydrous salts, when brought in contact with a certain quantity of water, are first converted into definite hydrates, and become very hot; but the subsequent solution of these hydrates in a larger quantity of water is attended with reduction of temperature. The solution of one liquid in another takes place without change of temperature, excepting when a definite compound is first formed, as on mixing oil of vitriol with water, in which case heat is evolved. (See HEAT, iii. 79, 109; also *Gmelin's Handbook*, ii. 69.—Favre and Silbermann, Compt. rend. xxiv. 1081; Jahresb. 1847-48, p. 53.—Favre, Compt. rend. l. 1150; lii. 316; Jahresb. 1860, p. 33.—Pohl, J. pr. Chem. lxxxii. 254; Jahresb. 1860, p. 36.—Hausmann, Jahresb. 1864, p. 97).—On the depression of temperature consequent on the dilution of saline solutions, see J. Regnauld (Instit. 1864, p. 158; Jahresb. 1864, p. 99).

The manner in which the solubility of a solid in a liquid is related to the chemical composition of the two, has not yet been reduced to any definite laws. As a general rule, it may perhaps be stated that solids dissolve with the greatest facility in those liquids which they most resemble in composition. Thus, metallic salts are for the most part more soluble in water than in alcohol or ether; whereas fats, resins, and many other organic bodies, dissolve more easily in alcohol, ether, benzene, oils, &c. than in water. But solids of strictly analogous constitution dissolve in the same liquid with very different degrees of facility. Thus, sulphuric acid forms a great number of salts which are soluble in water, and, on the other hand, baryta, lime, and magnesia form soluble salts with many acids; but barytic sulphate is one of the least soluble salts known, and calcic sulphate is but slightly soluble in water, whereas magnesic sulphate is very soluble.

The facility with which a solid dissolves in a liquid is not always proportional to the amount which the liquid is ultimately capable of dissolving, for it depends in a great measure on the physical condition of the solid, and on the manner in which it is brought in contact with the liquid. Pulverisation, by increasing the number of points of contact, of course facilitates solution. If the solid is placed at the bottom of the liquid, it dissolves with comparative slowness, because the solution formed immediately around the solid, being heavier than the supernatant liquid, remains at the bottom, and protects the solid from the further action of the liquid: the solution will therefore be facilitated by stirring the liquid, or by heating it at the bottom, so as to produce upward and downward currents. In many cases it is best to suspend the solid in the upper part of the liquid in a basket, or perforated box, so that the solution as it forms may fall to the bottom, and enable fresh liquid to come in contact with the solid. This plan is adopted in many manufacturing operations, as in lixiviating ball-soda, crude nitre, borax, &c.

Many substances, when immersed in a solvent, absorb a certain quantity of it, and are converted into tenacious lumps very difficult to dissolve; this is especially the case with resinous bodies. In such cases, it is often advantageous to mix the body with an insoluble substance, such as sand or pounded glass, to prevent the caking together, and enable the solvent to penetrate more easily to all parts of the solid.

The solubility of a solid in a liquid increases, for the most part, with rise of temperature; and for each particular temperature there is a certain limit, called the **point of saturation**, beyond which the liquid is incapable of taking up any more of the solid. The rate of increase is very different for different substances, and does not appear to be reducible to any regular law. Even the general law of increased solubility with rise of temperature admits of many exceptions: thus, lime-water saturated at 0° contains nearly twice as much lime as can be dissolved by the same quantity of water at 100°. Calcic sulphate also is more soluble in cold than in boiling water, and quite insoluble in water at 120°; sodic sulphate is more soluble in water at 33° than at other temperatures, either above or below, and has about the same degree of solubility at 0° as at 100°. Many other salts also exhibit a point of maximum solubility at some particular temperature, generally above the boiling-point of water. (HEAT, iii. 79.)

A saturated solution of a salt at any particular temperature may be obtained, either by heating an excess of the salt with water to a higher degree, and leaving the solution to cool to the required temperature, or by immersing an excess of the salt in cold water and slowly heating the liquid to the same point.

In the case of salts which, like saltpetre, do not contain water of crystallisation, and of many hydrated salts, the saturated solution contains the same quantity of salt, by whichever method it is prepared. But when certain hydrated salts—especially those which, like sodic sulphate and neutral sodic carbonate, are capable of crystallising with more than one proportion of water—are dissolved to saturation in hot water, and the solutions are left to cool slowly and quietly in a closed vessel, they often retain, after cooling to a certain temperature, a much larger quantity of the salt than the same quantity of water would be capable of taking up if originally placed in contact with the salt at that temperature. Such solutions are said to be **supersaturated**. They retain their excess of salt so long as they are left at perfect rest, and not cooled too low; but if stirred or agitated, or brought in contact with air containing particles of dust, or with a crystal of the same salt, or cooled down to a certain temperature, they suddenly deposit the excess of salt in crystals, exhibiting at the same time a considerable rise of temperature. This sudden crystallisation, if not produced by cold, appears to depend essentially on contact of the solution with small solid, perhaps crystalline particles; for it is not produced by passing air previously purified by oil of vitriol through the solution, or by agitation with a glass rod previously purified from dust by ignition (Löwel, Ann. Ch. Pharm. lxxvi. 227; Jahresb. 1850, p. 294; 1851, p. 331; 1852, p. 358.—Lieben, *ibid.* 1854, p. 322). According to Violette (Compt.

rend. lx. 831, 973; Jahresb. 1865, p. 74) and De Gernez (Compt. rend. lx. 833; lxi. 847; Jahresb. 1865, pp. 74, 78), the sudden crystallisation is in all cases induced only by contact with a crystal of the same salt, possessing the same form and degree of hydration as the crystals which separate out; and in the case of those supersaturated solutions which crystallise suddenly on exposure to the air, it is due to the presence of minute particles of that salt floating in the air. From an experiment of De Gernez, it appears that microscopic crystals of sodic sulphate may be obtained by passing air, even in the open country, through pure water, and evaporating the water on a glass plate. Jeannel (Compt. rend. lxi. 412; lxii. 37; Jahresb. 1865, pp. 77, 79), however, denies the necessity of contact with the salt actually contained in the solution. He finds, indeed, that a supersaturated solution of sodic acetate may be made to crystallise by contact with any solid substance (a piece of paper, for example), and a solution of sodic tartrate by contact with a clean dry glass rod. He attributes the phenomenon of supersaturated solutions chiefly to the fact, that the salts in question are capable of forming in hot water peculiar hydrates, which under certain circumstances remain permanent after the solution has cooled to a certain point, but are, for the most part, broken up by contact with a solid body, and especially with a particle of the dissolved salt. (Respecting supersaturated solutions of sodic carbonate and sulphate, see CARBONATES, i. 795, and SULPHATES.)

When two or more salts are dissolved in water, and no new salt separates out by double decomposition, the quantity of each held in solution by a given quantity of water is generally, but not always, less than if either salt were dissolved separately. In this case the quantities contained in a saturated solution are the same, whether the two salts are dissolved simultaneously in the water, or the water is first saturated with the one salt, and then brought in contact with an excess of the other, a portion of the first salt then crystallising out. A saturated solution of common salt shaken up with sal-ammoniac takes up a large quantity of the latter, and deposits some of the sodic chloride in cubes; a saturated solution of sal-ammoniac also takes up common salt, and deposits sal-ammoniac in dendritic forms. When a solution of common salt saturated at ordinary temperatures is mixed with a saturated solution of sal-ammoniac, a mixture is formed, without change of temperature, which is capable of taking up a certain quantity both of common salt and of sal-ammoniac. On warming the saturated mixture with common salt, a small quantity is also taken up, and separates out again on cooling. If, on the other hand, sal-ammoniac be added during the warming of the mixture, it at first dissolves, forming a clear solution; if a larger quantity be added, this also dissolves, but separates a considerable quantity of common salt; and as the liquid cools, the common salt redissolves, and the sal-ammoniac which had been taken up by the hot liquid crystallises out. Similar relations are exhibited by mixtures of sal-ammoniac and chloride of potassium, of the latter with chloride of sodium or barium, and apparently also by nitrate of ammonium and nitrate of sodium.

Many salts dissolve in water to the same amount, whether the water is shaken up with an excess of either of them alone, or simultaneously with a second salt; but the quantity of this second salt dissolved, is smaller than if the first were not present. Thus a saturated solution of potassic chloride, or nitrate, dissolves only a small quantity of potassic sulphate; and if a saturated solution of the latter be shaken up with either of the preceding salts, a large quantity of potassic sulphate separates out.

Lastly, a given quantity of water can in some cases dissolve a larger quantity of a salt (*A*), if previously saturated with another salt (*B*), and at the same time take up an additional quantity of the second. In this case the quantities taken up are different according as:

α. A quantity of water saturated with a salt *A* are shaken up with an excess of *B*.
β. Water previously saturated with *B* is saturated with *A*.
γ. The water is shaken up with an excess of the two salts simultaneously.

For example, with sal-ammoniac (*A*) and saltpetre (*B*), dissolved in water at 18¾°, the following quantities are taken up in the three cases by 100 pts. of water:

	α.	β.	γ.
Sal-ammoniac . .	37·98	44·33	39·84
Saltpetre . . .	37·68	30·56	38·62

In solutions containing three salts, still more complicated relations are observed, and in all cases, the effects produced are such as indicate the formation of double salts, and the division of the acids among the several bases. (CHEMICAL AFFINITY, i. 863; *Handw. d. Chem.* ii. 2^{te} Aufl. ii. [1], 554.—*Gmelin's Handbook*, ii. 71.)

On the questions whether certain salts dissolve in water in the anhydrous or hydrated state, see Schiff, Ann. Ch. Pharm. cvii. 293; Jahresb. 1858, p. 37.—Wüllner, Pogg. Ann. ciii. 529; cx. 564; Jahresb. 1858, p. 45; 1860, p. 47.—Rüdorff, Jahresb. 1862, p. 22.

On the supposed influence of gravity on the homogeneity of solutions: *Gmelin's Handbook*, i. 111.—Debus, Jahresb. 1853, p. 310.—Gale, Jahresb. 1855, p. 269.—Lieben, Ann. Ch. Pharm. ci. 77; Jahresb. 1857, p. 67.

On the solubilities of different salts, and the relations between the strength and specific gravity of saline solutions, see Michel and Krafft, Ann. Ch. Phys. [3], xli. 471; Jahresb. 1854, p. 295.—Kremers, Pogg. Ann. lxxxv. 37, 246; lxxxvi. 375; xcii. 497; xcv. 110; xcvi. 39; xcvii. 1; xcix. 25, 58, 435; ciii. 57; civ. 133; Jahresb. 1852, pp. 14, 305; 1854, p. 294; 1855, p. 294; 1856, p. 274; 1857, p. 67; 1858, p. 39.—Gerlach, Jahresb. 1859, p. 42.—Alluard, Ann. Ch. Pharm. cxxxiii. 292; Jahresb. 1864, p. 93.—G. J. Mulder, Jahresb. 1863, p. 92.—Girardin, Jahresb. 1865, p. 67.

On the solubility of certain salts in aqueous alcohol: A. Girardin, Ann. Ch. Phys. [4], v. 129; Jahresb. 1865, p. 64.

On the solubility of a substance in a mixture of its different solvents: Girardin, Compt. rend. xlv. 142; Jahresb. 1862, p. 57.

On the expansion of saline solutions: Kremers, Pogg. c. 394; cv. 360; cviii. 115; cxi. 60; cxiv. 41; Jahresb. 1857, p. 68; 1858, p. 41; 1859, p. 48; 1860, p. 46; 1861, p. 60.—Gerlach, Jahresb. 1859, p. 46.—Sorby, Phil. Mag. [4], xviii. 81; Jahresb. 1859, p. 50.

On the boiling-points of saturated solutions: Kremers, Jahresb. 1856, p. 275.

On the temperature and tension of the vapours given off from saline solutions: Babo, Jahresb. 1847–48, p. 93; 1857, p. 92.—Wüllner, Pogg. Ann. ciii. 529; cx. 387, 564; Jahresb. 1858, p. 42; 1860, p. 47.—E. Gerland, Pogg. Ann. cxxiv. 179; Jahresb. 1865, p. 71.

On the influence of pressure on solubility: Sorby, Proc. Roy. Soc. xii. 538; Phil. Mag. [4], xxvii. 145; Jahresb. 1863, p. 96.

On the index of refraction of saline solutions: Beer and Kremers, Pogg. Ann. ci. 133; Jahresb. 1857, p. 691.—Grailich and Handl, Wien. Akad. Ber. xxv. 515; Jahresb. *ibid.*—Kremers, Pogg. Ann. cvi. 586.—Pichot, Compt. rend. xlviii. 1118; Forthomme, Ann. Ch. Phys. [3], lx. 307.

On the molecular rotatory power of certain saline solutions: Arndtsen, Ann. Ch. Phys. [3], liv. 403; Jahresb. 1858, p. 49.

On the influence of temperature on the colour of saline solutions: Gladstone, Phil. Mag. [4] xiv. 423; Jahresb. 1857, p. 71.—Babo, Jahresb. 1857, p. 72.—Schiff, Ann. Ch. Pharm. cx. 203; Jahresb. 1859, p. 52.

On the coloration of saline solutions at various degrees of dilution: Gladstone, Phil. Mag. [4] xvi. 66; Jahresb. 1858, p. 47.

On the influence of coloured saline solutions on the spectrum (*ibid.*).

On the freezing of saline solutions: Dufour, Jahresb. 1860, p. 44.—Fritzsche, N. Petersb. Acad. Bull. vi. 385, 495; Jahresb. 1863, p. 97.—Rüdorff, Pogg. Ann. cxvi. 55, cxxii. 337; Jahresb. 1862, p. 20; 1864, p. 94.

On the diffusion of saline solutions, see LIQUIDS, DIFFUSION OF, iii. 705.

SOMERVILLITE. A variety of mellilite from Vesuvius (iii. 870).

SOMBRERITE. An earthy mineral, consisting mainly of calcic and aluminic phosphates, occurring on some of the small islands of the Antilles, chiefly on Sombrero. It contains, according to Phipson (Chem. Soc. J. xv. 277; Chem. News, ix. 28), 65 per cent. tricalcic phosphate, 17 aluminic phosphate, and 9 water, besides calcic sulphate, carbonate, &c.—a composition which may be approximately represented by the formula $8(3Ca''O.P^2O^5).(2Al^2O^3.3P^2O^5).20H^2O$. According to Julien, however, (Chem. News, ix. 16), it is not of constant composition.

SOMMITE. Syn. with NEPHELIN, from Somma (iv. 30).

SONCHUS. *Sow-thistle.*—A genus of cichoraceous plants. *Sonchus arvensis*, gathered during flowering-time, yields 86·0 per cent. water, and 1·19 ash; the plant also contains a bitter principle, wax, resin, a small quantity of free acid, &c. *S. oleraceus* yields, at flowering-time, 90·0 per cent. water, and 1·48 ash. The ashes of the two species were found by C. Sprengel (J. techn. Chem. ix. 17; x. 36) to contain, besides alumina and ferric oxide:

	K^2O.	Na^2O.	CaO.	MgO.	SiO^2.	SO^3.	P^2O^5.	Cl.	
S. arvensis .	21·9	13·7	27·0	4·6	3·0	15·1	8·6	6·0	= 99·9
S. oleraceus .	29·3	18·6	18·8	1·6	2·8	6·1	15·3	7·4	= 99·9

SONORA GUM. A kind of lac produced by the puncture of a coccus in *Mimosa cerifera*, a tree growing in Mexico. It appears to have been long used in Mexico as an irritant.

SOORANJEE. The root of *Morinda citrifolia* (iii. 1048).

SORBAMIDE. $C^6H^9NO = \left.\begin{matrix}C^6H^7O\\H^2\end{matrix}\right\}N$.—An amide produced by the action of dry ammonium-carbonate on crude sorbic chloride, or of aqueous ammonia on sorbic ether at 120°. It forms white easily fusible needles, soluble in water and in alcohol. (Hofmann.)

SORBANILIDE or *Phenyl-sorbamide*, $C^6H^8(C^6H^5)NO$, is produced by the action of aniline on sorbic chloride, as an oil which solidifies in the crystalline form. (Hofmann.)

SORBIC ACID. $C^6H^8O^2 = \left.\begin{matrix}C^6H^7O\\H\end{matrix}\right\}O$. (A. W. Hofmann, Chem. Soc. Qu. J. xii. 43.)—A monobasic acid, produced by isomeric transformation of parasorbic acid, a volatile oily acid obtained from mountain-ash berries. When the liquid which remains after partially saturating the juice of the unripe berries with milk of lime, is left to stand till all the neutral calcic malate is deposited from it (iii. 789), and then distilled in a copper vessel, ultimately with addition of a little sulphuric acid, an acid distillate is obtained, from which, after saturation with sodic carbonate and evaporation, a brown oil is separated by sulphuric acid; and by dissolving this oil in ether, leaving the ether to evaporate, and rectifying, a transparent colourless oil is obtained, consisting of parasorbic acid, $C^6H^8O^2$, which when gently heated with solid caustic potash, or boiled for some time with strong hydrochloric acid, is transformed into crystallisable sorbic acid, having the same composition.

Sorbic acid is easily purified by recrystallisation from hot water; it dissolves easily also in alcohol and ether, and crystallises from a boiling mixture of 1 vol. alcohol and 2 vols. water, in white needles an inch long. It is inodorous, melts at 134·5°, volatilises without decomposition, and decomposes carbonates. With *phosphoric chloride* it yields sorbic chloride, C^6H^7OCl. Heated with hydrate of barium, it yields a volatile aromatic hydrocarbon, together with carbonate of barium.

Sorbate of Ammonium crystallises in long needles: its concentrated solution is precipitated by chloride of calcium and by most salts of the heavy metals, but not by chloride of barium, strontium, or magnesium.—The *potassium-* and *sodium-salts* crystallise with difficulty.—The *barium-salt*, $C^{12}H^{14}Ba''O^4$, and the *calcium-salt*, $C^{12}H^{14}Ca''O^4$, crystallise in silvery scales.—The *silver-salt*, $C^6H^7AgO^2$, is a white crystalline precipitate.

Ethylic Sorbate or *Sorbic ether*, $C^6H^7(C^2H^5)O^2$, produced by passing hydrochloric acid gas into an alcoholic solution of the acid, or by the action of alcohol on sorbic chloride, is a liquid having an aromatic odour, like that of benzoic ether, and boiling at 195·5°.

Parasorbic Acid, $C^6H^8O^2$.—This acid, prepared as above, is when freshly distilled, a transparent colourless liquid, of specific gravity 1·068 at 15°. Its vapour, in the concentrated state, has a repulsive almost intoxicating odour: it is, in fact, the source of the peculiar pungent odour which the juice of mountain-ash berries evolves when partially saturated with lime. It boils constantly at 221°, but a portion of it is always converted during distillation, even in a stream of hydrogen, into a yellow resinous substance. It is faintly acid, dissolves in moderate quantity in water, forming an acid solution, and in all proportions of alcohol and ether. Its solutions in ammonia, potash, soda, baryta-water, and lime-water, dry up to amorphous residues; it dissolves in alkaline carbonates, but without expelling the carbonic acid.—*Nitrate of silver* added to the ammoniacal solution forms a white gelatinous precipitate, $C^6H^7AgO^2$, which blackens on exposure to light.

SORBIC CHLORIDE. *Chloride of Sorbyl*, C^6H^7OCl.—Produced by the action of phosphoric chloride on sorbic acid or its potassium-salt. It is converted by water into the acid, by alcohol into ethylic sorbate, by ammonia into sorbamide, by aniline into phenyl-sorbamide.

SORBIC ETHER. Ethylic sorbate.

SORBITARTARIC ACID. An acid produced by heating sorbite with tartaric acid to 100°. (Berthelot.)

SORBITE. *Sorbin*. $C^6H^{12}O^6$. (Pelouze, Ann. Ch. Phys. [3], xxxv. 292.)—An unfermentable sugar, isomeric with grape- and milk-sugar, existing in the ripe juice of mountain-ash berries. The expressed juice of the berries, gathered towards the end of September, produces deposits and vegetations when left to itself for 13 or 14 months, and at last becomes clear again; and the clear liquid, decanted and evaporated to a thick syrup, yields repeated crops of crystals, which are obtained pure by two crystallisations with help of animal charcoal.

Sorbite forms very fine, regular, transparent crystals, which, according to Berthelot, belong to the trimetric system, and are for the most part rhombic octahedrons:

$\breve{P}\infty$. $P\infty$. with oP ; over oP the angle $\breve{P}\infty : \breve{P}\infty = 38° 49'$; $\bar{P}\infty : \bar{P}\infty = 37° 7'$. The faces between oP and $P\infty$ are truncated by m$\bar{P}\infty$ (m$\bar{P}\infty : \bar{P}\infty = 164° 20'$). The crystals have a specific gravity of 1·654 at 15° ; they grate between the teeth, and are as sweet as cane-sugar. Optical rotatory power, for the transition-tint = 46·9° at 7°, only slightly variable with the temperature, and just as great in a recently prepared solution as in one that has been kept. (Berthelot, *Chim. organ.* ii. 252.)

Sorbite dissolves in about ½ pt. cold water; the saturated solution has a specific gravity of 1·372 at 15°. It is insoluble in cold, slightly soluble in boiling alcohol.

Sorbite forms with *chloride of sodium*, a compound crystallising in cubes.—Aqueous sorbite dissolves *hydrate of calcium* and *hydrate of barium*. The solution of the former deposits flocks when heated, decomposition occurring at the same time.—Aqueous sorbite dissolves *oxide of lead*; it does not precipitate basic acetate of lead, but on addition of ammonia throws down a white precipitate, which, while being dried, smells of caramel, and contains 79·4 per cent. lead (Pelouze).—Aqueous sorbite also dissolves *cupric hydrate*.

Sorbite when heated gives off acid water, and is converted after some time, at 150°—180°, into a dark-red mass consisting of sorbitic acid (Pelouze's sorbic acid). When quickly heated on platinum-foil, it melts and burns away with a smell of caramel. Hot *nitric acid* converts it into oxalic acid (Pelouze). Oxidising agents also produce racemic acid from sorbite (Dessaignes, Bull. Soc. Chim. 1861, p. 32). It is not altered when heated with *dilute acids*; it is coloured reddish-yellow by *oil of vitriol*, charred on heating. When heated for several hours with fuming *hydrochloric acid*, it is converted into humous substances in the same way as glucose (p. 315). (Berthelot, *Chim. organ.* ii. 252.) Sorbite, heated to 100° with *tartaric acid*, yields a small quantity of a substance belonging to the class of saccharides (p. 316), whose calcium-salt reduces potassio-cupric tartrate (Berthelot). It turns brown when heated with *potash-ley*, and evolves a smell of caramel. Heated with *lime*, *hydrate of barium*, or *oxide of lead*, it behaves in the same way. The solution of *cupric hydrate* in aqueous sorbite, and aqueous solution of sorbite mixed with *potassio-cupric tartrate*, deposit cuprous oxide when warmed or left to stand. Sorbite is not fermentable with *yeast* (Pelouze), not even after being heated with acids; but when left to stand in contact with *cheese* and *chalk*, at 40°, it suffers a decomposition, which gives rise to a large quantity of lactic acid, alcohol, and butyric acid, without previous formation of a fermentable sugar. (Berthelot.)

SORBITIC ACID. Pelouze's *Sorbic Acid.*—An acid obtained by heating sorbite for some time to 150°—180°. On dissolving the residue (which is insoluble in water, aqueous acids, or alcohol), in aqueous ammonia or potash, a dark-brown solution is obtained, from which hydrochloric acid throws down amorphous dark-red flakes; these contain, after drying between 120° and 150°, 57·96 per cent. C, 5·51 H, and 36·53 O, corresponding, according to Pelouze, with the formula $C^{32}H^{18}O^{15}$. Their solution in ammonia-water gives coloured precipitates with metallic salts; with lead-salts one containing 51·35 per cent. lead-oxide, $C^{32}H^{18}O^{15}.3PbO$, according to Pelouze.

SORBUS AUCUPARIA. *Pyrus Aucuparia. Mountain-ash. Rowan-tree. Sorbier. Vogelbeerbaum.*—A pomaceous tree, the unripe berries of which contain large quantities of free vegetable acids—viz. citric, tartaric, and malic acids; the last is most abundant when the berries have a rose-red colour; previously to this, the tartaric acid predominates, and later in the season the malic acid likewise disappears. The juice of the berries contains also a non-fermentable sugar, viz. sorbite, together with fermentable sugar; for the juice even of unripe berries has been found to pass into spontaneous fermentation, and to yield, from 100 vols., 4 vols. of spirit containing 50 per cent. alcohol. After the spirit there distils a milky liquid, which, after a few days, deposits a small quantity of a stearoptene in small shining crystals (Liebig). Brandy is prepared from the juice of the ripe berries in the Tyrol, in North Germany, and other places.

The juice likewise contains a pungent-smelling oily acid (*parasorbic acid*, p. 352), which may be separated by distillation after the malic acid has been precipitated by lime.

The flowers of the mountain-ash, and the bark of the stem and root, are said to yield, by distillation with water, products containing hydrocyanic acid; the bark also tannin and a bitter principle. (Gössmann.)

SORBYL. C^6H^7O. The hypothetical radicle of sorbic acid.

SORDAWALLITE. A mineral resembling pit-coal in appearance, forming three layers in trap near Sordawala in Finland, and associated with magnetic pyrites, at Bodenmais in Bavaria. Hardness = 2·5. Specific gravity = 2·53—2·58.

Gives off water when heated, and melts to a black bead before the blowpipe. Partially decomposed by acids. Analysed—*a.* by Nordenskiold (Schw. J. xxxi. 148);—*b.* by Wandesleben (N. Jahrb. Pharm. i. 32):

	P^2O^5.	SiO^2.	Al^2O^3.	Fe^2O^3.	FeO.	MgO.	H^2O.		
a.	2·68	49·40	13·80	. .	18·17	10·67	4·38	=	99·10
b.	2·26	47·70	16·65	24·32	. .	10·21	. .	=	98·14

The presence of phosphoric acid, and the uncertainty as to the state of oxidation of the iron, render it impossible to reduce these results to a definite formula.

SORGHO. *Sorghum saccharatum. Holcus saccharatus.* Sugar-sorgho. Chinese sugarcane. Imphee. Kao-lien.*—A sugar-producing grass, resembling maize in external appearance. It appears to have been first obtained by the Jesuit missionary Du Halde, from the Chinese province Le Chuen; the seed was sent to France in 1851, where the plant was cultivated, chiefly by Vilmorin and Beauregard, and exported in 1854 to the United States, where numerous experiments were made with reference to its utility for the manufacture of sugar, and in agriculture as a substitute for the ordinary green-crops. Its chemical composition has been investigated by Gössmann and other chemists; but it does not appear certain that all the experiments have been made on the same species of plant.

The stem or cane freed from leaves contains, according to Gössmann, 78·9 per cent. water, 10·2 soluble constituents, 8·2 cellulose, 0·4 to 0·5 insoluble salts and cerasin. This last is a waxy substance distributed unequally over the surface of the plant, but most thickly on those parts which are covered by the sheaths of the leaves; when mixed with tallow it is said to make excellent candles. By charring the defoliated cane, Gössmann obtained 0·71 per cent. inorganic constituents. The residue, which was alkaline, consisted of calcic and magnesic phosphates, calcic, magnesic, potassic, and sodic carbonates and chlorides, and silica; the potash was in larger proportion than the soda.

The leaves, which contain no sugar, leave when burnt, 2·07 per cent. inorganic constituents, chiefly consisting of silica, lime, and magnesia, and contain 27 per cent. moisture.

The ash-constituents of the entire plant have been determined by J. Elwert. The plants used in this investigation belonged to a species of sorgho, called *broom-corn*, cultivated in America, and distinguished from the Chinese sugar-cane by its longer and much-divided panicle. 100 kilogrames of the green plant, equivalent to 15·5 kilogrammes of the dry plant, yield 1·379 kilogrammes ash, consisting of—

K^2O.	Na^2O.	CaO.	Cl.	SO^3.	P^2O^5.	CO^2.	Si^2O.	X.†		
20·3	4·7	21·4	2·2	1·9	8·0	14·1	16·5	10·5	=	99·6

Of these there are soluble in water—

K^2O.	Na^2O.	Cl.	SO^3.	P^2O^5.	SiO^2.
20·3	4·7	2·2	1·9	3·4	3 3

soluble in hydrochloric acid: 21·4 CaO, 14·1 CO^2, 4·6 P^2O^5; insoluble: 13·2 silica, and 10·5 sand.

The juice obtained by pressing the plant tastes very sweet, has a greenish-yellow colour, turbid appearance, faint acid reaction, and a specific gravity of about 1·07 (9° to 9½° B.) at 19°. It boils at 101°—101·5°, and between 60° and 70° begins to deposit an albuminous coagulum, without however clarifying completely, an effect which takes place only after prolonged boiling. When left to itself, at 20° to 25°, it soon begins to ferment. When evaporated, it leaves—after the albuminous constituents have been skimmed off—a transparent, viscid, sweet residue, which exhibits no trace of crystals, and, if somewhat unripe plants have been used, gives the reactions of starch. From perfectly ripe canes Gössmann obtained nothing but cane-sugar, and that to the amount of 9 to 9·56 per cent. According to Reihlen and Fehling, the juice of broom-corn, not quite ripe, contains 4 per cent. cane-sugar, and 10 per cent. uncrystallisable sugar. Lüdersdorff found in the juice of the Chinese sugar-cane, 7·5 per cent. sugar, consisting of equal parts of cane-sugar and fruit-sugar; and Bergemann found in it no cane-sugar, but 11·3 per cent. fruit-sugar. Hence, and from the elaborate experiments of Dr. Jackson (Polyt. Centralbl. neue Folge, xii. 1649), it appears that the plant, in its earlier stages of development, contains only grape-sugar, together with starch; but when it ripens, all the starch disappears, and nothing but cane-sugar is present. Of indifferent substances, the juice contains mucous nitrogenous matters, chlorophyll, gum, and albuminous compounds. The quantity of the latter, though not very great, is sufficient to convert the whole of the cane-sugar into glucose, and to resolve the latter into alcohol and carbonic anhydride. According to Löffler, the juice also contains two peculiar vegetable acids.

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* Henry S. Olcott, *Sorgho and Imphee, the new Chinese and African Sugarcanes*, New York, 1857.—Vilmorin, *Recherches de sorgho sucré*, 1854.—Stansbury, *The Chinese Sugar-cane*, New York. 1857.—James F. C. Hyde, *The Chinese Sugarcane*, Boston, 1857.—J. Lovring, *The Chinese Sugarcanes*, Philadelphia, 1858.—A. Gössmann. *Journ. f. Landwirthschaft*, von Henneberg, neue Folge, i 294 (1868).—Habich, *Polyt. Centralbl.* 1858, p. 1647.—Löffler, *Das Chinesische Zuckerrohr*, Braunschweig, 1859.—*Handw. d. Chem.* viii. 68.

† Sand with traces of iron.

Olcott found in the juice 15·2 per cent. sugar, 1·0 salts and organic constituents (albumin, vegetable fibre, gum, chlorophyll, &c.), and 83·8 water. The salts were found to consist of 0·750 potassic carbonate, acetate, chloride, and sulphate, 0·218 acid calcic and magnesic phosphates, and 0·012 silicic hydrate, mixed with ferric and manganic oxides.

The ash of the juice contains, according to Gössmann, 0·0015 per cent. silica, together with the following constituents soluble in water:—0·219 calcic and magnesic phosphates, with traces of iron; 0·310 alkali, chiefly potash; 0·69 sulphuric anhydride, 0·065 chlorine, and 0·079 phosphoric anhydride (= 0·742). The juice probably also contains small quantities of oxalic and tartaric acids.

The expressed plants (*begasse*), which may be used for paper-making, contain, according to Olcott, 1·6 per cent. ash, consisting of—

K^2SO^4.	Na^2SO^4.	CaO.	MgO.	SO^3.	P^2O^5.	Cl.	SiO^2.	X.*	
8·10	9·60	11·80	9·30	28·70	14·42	3·70	14·40	0·68	= 100

The seed of sorgho is yellowish, and yields a white flour, used in Marseilles and Lyons for the finer sorts of bread and biscuits. It is rich in starch and fat, and contains, according to Olcott, from 10 to 12 per cent. nitrogenous substances, and 60 to 66 per cent. starch. The seeds boiled with 12 to 15 pts. water form a glutinous paste; when exhausted with ether, they yield a not inconsiderable quantity of fat. From 50 to 60 grammes of the ground seeds Gössmann obtained several grammes of solid fatty acid.

When animals are fed on the seed, their bones gradually acquire a red colour.

The glumes (floral leaves) and stems of sorgho contain red colouring-matters, which may be used for dyeing silk and wool.

SPADAITE. A hydrated magnesic silicate occurring, together with wollastonite, at Capo di Bove, near Rome. It is amorphous, has a conchoïdal to splintery fracture, bluish-red colour, and slightly waxy micaceous lustre. Hardness = 2·5. Gives off water when heated, and melts before the blowpipe to a glassy enamel. Dissolves in strong hydrochloric acid, the silica easily gelatinising. Contains, according to v. Kobell (J. pr. Chem. xxx. 467), 56·00 per cent. silica, 0·66 alumina, 30·67 magnesia, 0·66 ferrous oxide, and 11·34 water (= 99·33), which may be represented, approximately, either by $5Mg''O.6SiO^2.4H^2O = Mg''Si^2O^5.4Mg''SiO^3.4H^2O$, or by $6Mg''O.7SiO^2.4H^2O = Mg''Si^2O^5.5Mg''SiO^3.5H^2O$.

SPÄNKÅDA. *Tuggkåda.*—A resin much used in Northern Sweden for chewing, and said to keep the teeth clean and the mouth cool. It collects in lumps on the stems of pine-trees, and is difficult to separate from the pine-resin, which it resembles. It is separated from adhering bark by kneading under warm water.

This resin is brownish without, with a rose-red tinge, yellowish-brown within, becomes darker and reddish on exposure to the air. It is brittle at ordinary temperatures, and when chewed softens at first, exhibiting a sour and balsamic taste; by continued chewing it becomes rose-red and brittle. It contains a small quantity of a viscid volatile oil, quite distinct from oil of turpentine, which may be separated by distillation with water; also several resins, and a crystallisable easily alterable acid, which may be extracted by water. This acid is soluble in alcohol, forms soluble salts with the alkalis and alkaline earths; precipitates ferric chloride completely; forms a dingy-green precipitate with cupric acetate, sulphur-yellow with basic acetate of lead, even in dilute solution; with the neutral acetate also in concentrated solution; white with nitrate of silver.

The resin, after exhaustion with water, dissolves completely in alcohol of specific gravity 0·84, but not completely in ether; water added to the alcoholic solution throws down a powder, which can no longer be masticated. Potash unites with the resin, forming with one portion of it, a compound insoluble in excess, with the remainder a soluble compound; the latter resin is also soluble in ammonia. (Berlin, Ann. Ch. Pharm. lii. 404.)

SPANIOLITE. Von Kobell's name for certain varieties of tetrahedrite containing mercury.

SPANIOLITMIN. A non-azotised colouring-matter, occurring, according to Kane, in small quantity in litmus (iii. 731).

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* Ferric oxide, carbonic anhydride, and loss.

SPARTAITE. Breithaupt's name for a variety of calcspar from New Jersey, which, according to Jenzsch (Pogg. Ann. xcvi. 145), has a specific gravity 2·81, hardness 3·5, and contains 80 per cent. calcic carbonate, together with the carbonates of magnesium, manganese, iron, and zinc, and 5·3 per cent. calcic fluoride.

SPARTALITE. Native oxide of zinc, usually coloured red by admixture of manganic oxide. (See ZINC.)

SPARTEINE. $C^{15}H^{26}N^2$. (Stenhouse, Ann. Ch. Pharm. lxxviii. 15; Pharm. Centr. 1851, p. 439; Chem. Gaz. ix. 117.—Gerhardt, *Traité*, iv. 236.—E. J. Mills, Chem. Soc. J. xv. 1; Gm. xiii. 151.)

History.—Sparteine was discovered in 1851 by Dr. Stenhouse, while investigating the *Spartium Scoparium*, or Common Broom. The formula proposed by Stenhouse was subsequently modified on theoretical grounds by Gerhardt, but a re-examination by Mills showed that Stenhouse's formula doubled represents the true composition of sparteine.

Preparation.—1. An aqueous decoction of broom is concentrated to about a tenth of its bulk, and set aside in a cool place for twelve hours; and the gelatinous mass which forms is thrown on a filter, and washed with cold water. The solutions contain the sparteine, while scoparin in an impure state remains on the filter. The filtrate is distilled with excess of soda, when a colourless basic oil slowly collects at the bottom of the aqueous liquid in the receiver. (Stenhouse.)

2. The plant is exhausted with water faintly acidulated with sulphuric acid; the extract, concentrated by evaporation, is distilled with soda until the distillate has no longer a bitter taste or alkaline reaction; the distillate, acidified by hydrochloric acid, is evaporated to dryness on a water-bath; and the mass, slightly moistened, is then distilled with solid hydrate of potassium. Ammonia is then given off, followed by the base in the form of a thick oil. The base is dehydrated by gentle heating with sodium in a current of dry hydrogen. When completely dry, the sodium remaining is removed, and the base is finally purified by rectification. (Mills.)

Properties.—Sparteine is a colourless, transparent, viscid oil. Its specific gravity does not appear to have been determined, but it is heavier than water. It has a peculiar odour, which is more unpleasant after rectification. It has a very bitter taste. It boils at 288°. (The high boiling-point suggests the idea of its being a diamine). It neutralises acids, but the salts formed crystallise with difficulty. It is a narcotic poison of the nicotine character, but inferior in energy. One drop dissolved in acetic acid, and administered to a rabbit, first produces excitement; but this is followed by stupor, lasting for five or six hours. Four grains are sufficient to kill a large rabbit. It readily forms double salts with the chlorides of the heavy metals.

Sparteine dissolves sparingly in water, but may be separated by adding chloride of sodium to the solution. Most of its physical properties, including its vapour-density, have yet to be determined.

Decompositions.—1. Sparteine becomes brown on exposure to the air for a few days at ordinary temperatures, and more rapidly while boiling.—2. Boiled with *hydrochloric acid*, it is decomposed, yielding a solution having an odour of mice (Stenhouse). On the other hand, Mills concentrates weak solutions of sparteine by saturating with *hydrochloric acid*, and evaporating to dryness on the water-bath.—3. *Nitric acid* decomposes sparteine, yielding a substance which, when treated with *chloride of lime*, affords chloropicrin.—4. *Bromine* converts sparteine into a brown resinous substance, much heat being developed during the reaction.

Salts of Sparteine.—The *chloride*, *bromide*, and *iodide* are amorphous and unfit for analysis. (Mills.)

The *oxalate* forms acicular crystals, which are difficult to obtain.

Chloroplatinate, $C^{15}H^{26}N^2.2HCl.Pt^{iv}Cl^4.2H^2O$.—This salt precipitates as a yellow crystalline powder when a solution of tetrachloride of platinum is added to a solution of sparteine in hydrochloric acid. It crystallises readily from a solution in hot hydrochloric acid.

Chloroaurate, $C^{15}H^{26}N^2.2HCl.Au'''Cl^3$.—Sparteine also forms double salts with iodide and chloride of zinc.

Substitution-derivatives of Sparteine.

Iodide of Ethylsparteine, $[C^{15}H^{27}(C^2H^5)N^2]'I^2$.—Equal volumes of sparteine, alcohol, and iodide of ethyl are to be heated together in sealed tubes for an hour to 100°. The mixture becomes dark-coloured, and deposits the ethylated compound in crystals. They are sparingly soluble in cold, readily in hot alcohol, and excessively soluble in hot water (Mills). Oxide of silver transforms the iodide of ethylsparteine into the hydrated oxide, $\left.\begin{matrix}[C^{15}H^{27}(C^2H^5)N^2]\\H^2\end{matrix}\right\}O^2$. (Mills.)

Hydrate of ethylsparteine, on treatment with alcohol and iodide of ethyl, in sealed tubes, yields iodide of diethylsparteine, $[C^{15}H^{26}(C^{2}H^{5})^{2}N^{2}]''I^{2}$. (Mills.)

Constitution of Sparteine.—It appears from the above researches that sparteine is a tertiary diamine, having the formula $(C^{15}H^{26})^{vi}N^{2}$, but, as with so many of the natural alkaloïds and also of those formed by destructive, distillation, nothing definite is known of the hydrocarbon group which replaces the hydrogen in the typical ammonia. C. G. W.

SPARTIUM. A genus of plants belong to the papilionaceous group of the leguminous order. *Sp. monospermum* is said, by Lorenzo and Moreno (J. Chim. med. ix. 747), to yield a crystalline substance, spartiin, analogous to salicin.

The common broom (*Spartium scoparium*, L., *Cytisus scoparius*, Link) has been examined by several chemists. Cadet (J. Pharm. x. 432) found in the flowers a volatile oil, fat, a light-yellow colouring-matter, and a peculiar substance soluble in water and alcohol, and having the taste and smell of the plant; Reinsch (Jahrb. pr. Pharm. xii. 141) found, in the flowers and green parts of the plant, a crystallisable bitter principle. Stenhouse (Phil. Trans. 1851, p. 422) obtained from the plant a crystalline colouring-matter, scoparin (p. 208), and a volatile base, sparteine; both these substances are most abundant in plants which have grown in sunny situations. According to C. Sprengel (J. techn. Chem. v. 129), 100 pts. of the green plant yield 0·615 pt. of ash free from carbonic acid, and containing 27·6 per cent. potash, 1·0 soda, 24·1 lime, 4·2 magnesia, 13·0 alumina, 5·7 ferric oxide, 0·7 manganic oxide, 9·7 silica, 1·4 chlorine, 0·1 sulphuric anhydride, and 12·3 phosphoric anhydride.

The root of the common broom has, according to Reinsch, a decided liquorice-taste, with irritating after-taste.

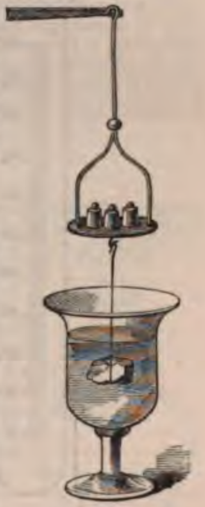
SPEAR PYRITES. Syn. with Marcasite (iii. 402).

SPECIFIC GRAVITY. By this term is understood the weight of a body as compared with that of an equal volume of another body assumed as a standard. It is, of course, necessary that the standard shall be readily obtainable in a pure state; distilled water is therefore employed for solids and liquids, and atmospheric air for gases and vapours. In certain scientific investigations it is not unfrequent to use hydrogen as the unit of density for gases and vapours. In this case it is usual to make the experimental comparison with air, and subsequently reduce it to that of hydrogen by calculation.

As the volumes of solids, liquids, and gases are affected by heat, it is absolutely necessary to perform the operations at known temperatures. It is usual in this country to make the experiment at 60° F. (= 15·5° C.) in the cases of solids and liquids; and with gases, to make the experiment at the temperature of the air at the time, and reduce the observed volume, by calculation, to the temperature of 15·5°. With vapours the experiment must be made at a temperature sufficiently elevated to ensure their obeying, within certain limits, the laws of permanent gases. The standard temperature in France is usually 0° for gases, and 4° (the point of maximum density of water) for solids and liquids.

We shall consider the methods of determining the specific gravities of solids, liquids, vapours and gases under separate heads:—

Fig. 750.



Specific Gravities of Solids.

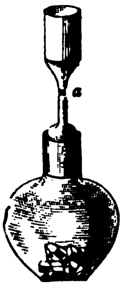
To determine the specific gravity of a solid, it is only necessary, in addition to its weight, to know that of an equal bulk of water. The method to be selected will depend upon the chemical and physical characters of the substance. We shall consider the following instances, which include all those which are likely to occur even in the investigation of the most troublesome organic substances:—

1. *The substance is solid, heavier than water, and insoluble in that liquid.*
2. *The substance is solid, and insoluble in, but lighter than water.*
3. *The substance is solid, heavier than water, but in fragments.*
4. *The substance is solid, heavier than water, but soluble in it.*
5. *The substance is solid, but soluble in and lighter in water.*

1. *The substance is solid, heavier than water. and insoluble in that liquid.*

a. By the Hydrostatic Balance.—The most usual and generally applicable method is by the use of a hydrostatic balance. The substance is first to be weighed accurately, in the usual manner. It is then to be attached by a slip-knot to a horsehair, and suspended from the short pan of a balance, as in *fig.* 750. A vessel of distilled water being so placed that the substance will hang freely in it, the substance will appear to be lighter than before, the loss of weight being exactly the same as the weight of a volume of water equal to that of the substance. In other words, a body immersed in water not only displaces its own volume, but also loses a portion of its weight exactly equal to that of the water displaced. If the arms of the balance are equal in length, it will only be necessary to place weights in the short pan until the equilibrium is restored, to get all the data necessary to enable the specific gravity to be computed. If the arms are unequal in length, it will be necessary to adjust the weights in the other pan until the substance is counterpoised. To calculate the density, it is only necessary to divide the weight in air by the loss of weight in water. Great care must be taken during the operation that the substance is always surrounded by water, that it does not touch the sides of the vessel, and that no air-bubbles adhere to it.

Fig. 751.

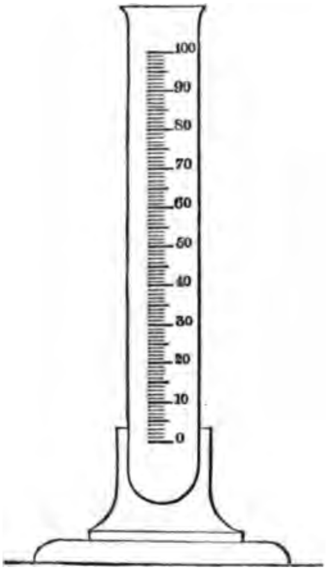


b. By Nicholson's Hydrometer. See HYDROMETER (iii. 211).

c. By the Flask.—A flask with a wide mouth and hollow stopper, enlarged at its upper extremity, and having a mark at *a* (*fig.* 751), is to be filled to the mark with water, and its weight is to be ascertained. The level of the liquid can easily be regulated by the aid of a small roll of filtering-paper. The stopper having been removed, the substance, the weight of which is known, is to be dropped in. The stopper is then to be replaced, care being taken that no air-bubbles either adhere to the substance, or lie between the stopper and the water; the level of the water having been again adjusted to the mark, the weight is to be ascertained. To calculate the result, we must add the weight of the substance to the weight of the flask of water, and from the number so obtained deduct the weight of the flask, &c., as obtained after inserting the substance. The difference will be the weight of a quantity of water equal in bulk to the substance. It is then only necessary to divide the original weight of the substance by the number so obtained.

d. Process by measuring the volume of the substance.—The substance is to be weighed in air, and then dropped into a graduated tube (*fig.* 752), filled to the zero of the scale with water. The graduations indicate grains (or grammes) of water. It is evident, therefore, that when the substance is inserted, the liquid will rise in the tube, and indicate at once the weight of a bulk of water equal to that of the substance. It is, therefore, only necessary to divide the weight in air by the weight of an equal volume of water, as indicated by the instrument, to obtain an approximation to the specific gravity.

Fig. 752.



2. *The substance is solid, and insoluble in, but lighter than water.*

a. The solution of this problem is excessively simple. Only three data are required, namely: the weight in air of the light substance $= P$; the weight *in water* of a piece of lead, or other heavy substance sufficient to sink it, $= P'$; and the weight *in water* of the light substance, and the lead attached to each other, $= P''$. We have then the density D by the following expression:

$$D = \frac{P}{P' - P'' + P}$$

Or, in words, deduct from the weight of the heavy substance, in water, the weight, in water, of the light and heavy substance attached; add to the remainder the weight of the light substance in air; and divide the weight of the light substance in air by the number so obtained: the result is the density.

b. The process by the flask is also applicable to this case. A vessel capable of being closed by a stopper being taken and weighed full of water, the light substance, if its physical condition permit, may be inserted after weighing; a quantity of water, equal in bulk to the substance, will then overflow; on replacing the stopper, and re-weighing, all the necessary data will be obtained, the calculation being made as in 1 c.

3. *The substance is solid, heavier than water, but in fragments.*

The process by the flask is especially applicable to this case. The operation and calculation are precisely as in 1 *c.*

4. *The substance is solid, heavier than water, but soluble in it.*

It is sometimes possible to varnish it very thinly, so as to prevent the access of the water, and to determine the specific gravity by the process 1 *a.* A serious error may, however, creep in if the varnish should penetrate any interstices in the substance. It is, therefore, in every way preferable to use the method 1 *a*, substituting for the water a liquid in which the substance is insoluble, making in the calculation a correction for the density of the liquid. Oil of turpentine, or benzene, will answer for most cases of this kind.

The calculation, which is extremely simple, is as follows:—From the weight of the substance in air, deduct the weight in the liquid; this gives the weight of a volume of the *liquid* equal to that of the substance. Then, to obtain the weight of a bulk of *water* equal to that of the substance, we say: As the specific gravity of the liquid, is to the specific gravity of water, so is the weight of a bulk of the *liquid* equal to that of the substance, to the weight of a bulk of water equal to that of the substance. The weight in air of the substance is then to be divided by the latter number. Or, more simply, calling the weight of the substance in air P, and the weight in the liquid P′, the weight of a bulk of the liquid equal to that of the substance will be $P - P' = P''$; and calling the density of the liquid S, and that of the water S′, we obtain the weight P‴ of a volume of water equal to that of the substance by the expression:

$$\frac{P'' S'}{S} = P'''$$

The density D of the substance therefore becomes:

$$D = \frac{P}{P'''}$$

The operation may also be made by the flask, a correction for the density of the liquid used being introduced into the calculation.

5. *The substance is solid, but soluble in and lighter than water.*

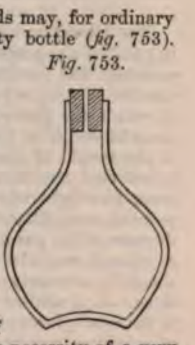
The process by the flask is specially adapted to this comparatively rare case. Benzene or turpentine is to be substituted for water, and the experiment is to be conducted as in 1 *c.* To obtain the weight of a bulk of water equal to that of the substance, we say: As the specific gravity of the liquid is to the weight of the liquid displaced, so is the specific gravity of water to the weight of a bulk of water equal to that of the substance. The weight of the substance in air divided by the latter number, of course gives the density required.

SPECIFIC GRAVITIES OF LIQUIDS.

a. By the Hydrometer. See HYDROMETER (iii. 205).

b. By the Specific Gravity bottle.—The specific gravities of liquids may, for ordinary purposes, be determined by means of the common specific gravity bottle (*fig.* 753). As ordinarily constructed by instrument-makers, it consists of a very thin glass flask, having a hollow stopper made from thermometer tube, carefully fitted by grinding. It is so constructed that, with the stopper in its place before adjustment, it holds a little less than 1000 grains of water. Enough of the under-surface of the stopper is then removed by grinding to allow of the bottle holding exactly that quantity at a temperature of 15·5° = 60° F. A counterpoise is also supplied having exactly the weight of the bottle. By this arrangement specific gravities may be readily obtained without calculation. If the bottle holds 1000 grains of water, it will hold 1850 grains of monohydrated sulphuric acid, 850 grains of benzene, &c., these numbers at once expressing the ratios of the densities.

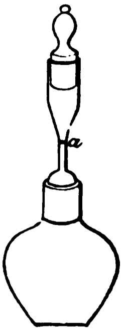
Fig. 753.



It is evident that the adjustment of the bottle to a capacity of 1000 grains of water has no advantage except that of saving the necessity of a very short calculation. Such a piece of apparatus has disadvantages which far more than counterbalance so slight a convenience. In the first place, it requires a quantity of liquid, which is often more than is at the disposal of the operator. In the next place, it has the serious drawback that, if the temperature of the balance-case be higher than that of the liquid, expansion of the latter takes place, and it rises in the tube and escapes down the sides of the flask. If, on the other hand, the temperature of the balance-case be lower, contraction ensues, and a void space is formed below the stopper, which cannot always be easily filled up. Moreover, volatile liquids escape by the aperture, rendering exact weighing excessively difficult. It would also be impossible, in such an apparatus, to determine the density of a liquid at a standard temperature either above or below that of the air at the time of making the experiment.

All the above objections are obviated by the use of the flask shown in *fig.* 754. It is essentially the same as that described in treating of the method of determining the specific gravities of solids by the flask, but furnished with a light well-fitting stopper having no aperture.

Fig. 754.



If it be required to determine the density of a very volatile liquid at (say) 4°, it is only necessary to fill the flask, a little above the mark *a*, first with pure distilled water, and subsequently with the liquid to be examined. After filling, it will be necessary, both with water and with the liquid, to keep the flask in a bath cooled to 4°, until the required temperature is obtained; the level at *a* may then be adjusted by the aid of a piece of filtering-paper. The stopper having been inserted, the apparatus is to be allowed to acquire the temperature of the laboratory, so as to prevent errors in weighing, which might arise from the deposition of moisture. The only effect, as regards the liquid, will be its rise in the tube, its escape being impossible owing to the enlargement. Volatilisation is also provided against by the stopper.

If, on the other hand, the determination is to be effected at a temperature above that of the atmosphere, the level is to be adjusted at the proper moment, and the apparatus may then be allowed to cool. The liquid will then descend in the tube at *a*; but no source of error is introduced if the stopper be removed for an instant to allow of the ingress of a proportional volume of air, and even this precaution is unnecessary save in refined experiments.

When the quantity of liquid to be operated upon is very small, a vessel of the above form, but of sufficiently small size, may easily be constructed at the blowpipe-lamp. Of course the flask will then be only in one piece; and if the liquid under examination be volatile, a small cork can be inserted, because, as the fluid is only allowed to rise to the mark on the neck, there will be no fear of errors arising from contact, and consequent absorption or chemical action.

Another method of determining the specific gravities of liquids, consists in weighing a piece of glass or platinum, first in water, and then in the liquid; the weights of equal volumes of the two liquids can thus be obtained with accuracy, even when working upon comparatively small quantities. It is not often, however, that this method possesses any great advantages over the others previously described.

For general considerations on specific gravity, as connected with atomic volume, see the article Atomic Volume (i. 440).

Specific Gravities of Gases.

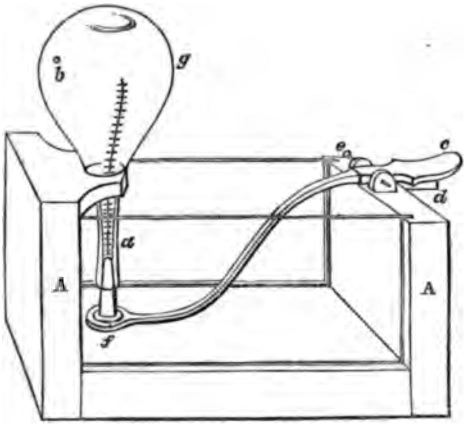
The determination of the specific gravity of a gas, so eminently simple in theory, is in practice an operation of the greatest delicacy. It is easy enough to obtain moderate accuracy, but results worthy to be depended on can only be procured by taking a number of minute precautions:—1. In the first place, it is important that the balloons in which the gases are to be weighed should be of such capacity that any minute error in weighing (such as a deci-milligramme) shall bear but a very small proportion to the weight of the gas, even if the latter be hydrogen itself.—2. Great care must be taken that the film of moisture which deposits upon the glass of the balloon is the same in weight when weighing the gas that it was when weighing the air. This is a point of great difficulty, and its neglect may give rise to serious errors.—3. The absolute dryness of the gas and the air, with the weight of an equal volume of which it is to be compared, must also be ensured.—4. The temperature must be most carefully noted, and should be as nearly as possible the same during all the weighings, so as to avoid corrections.—5. A similar remark applies to the pressure of the atmosphere, and consequently to the elastic force of the gas.—6. The balance should be of such delicacy that the errors of weighing have no appreciable influence upon the result.—7. Every possible care must be taken that the air and gas are absolutely pure.

There are three principal cases, which occur in laboratory practice, in which it becomes necessary to determine gaseous densities:—1. In the first, it is merely necessary to ascertain the specific gravity of a gas produced in a reaction, with a view to controlling or ascertaining its atomic weight.—2. It is often required to determine the specific gravity of coal-gas for technical purposes.—3. It is sometimes required to determine the specific gravity of a gas with every precaution, so as, in fact, to obtain a standard result. In the first and second cases, the process of Bunsen is unquestionably the best to be employed; in the third, it would be proper to use that of Regnault. We shall consider both of these methods, premising that for minute details it will be proper to consult the original works. (Bunsen's *Gasometry*, translated by Roscoe. Walton and Maberly.—Regnault, *Relation des expériences entreprises par ordre de M. le Ministre des travaux publics, et sur la proposition de la Commission Centrale des Machines à vapeur, pour déterminer les principales lois et les données numériques qui entrent dans le calcul des Machines à vapeur. Mémoires de l'Académie Royale des Sciences de l'Institut de France.*—Also Jamin, *Cours de Physique*, ii. 165.)

Bunsen's Method.

For the purpose of determining the specific gravity of a gas, Bunsen employs a light glass flask (*fig.* 755), of 200 or 300 cubic centimetres capacity, with a long narrow neck, having a millimetre scale etched upon it. It is furnished with an accurately-fitting glass stopper. The aperture of the neck is only about the thickness of a straw. Before filling the flask with gas, a small piece of fused chloride of calcium is dropped in, and made to crystallise on the side of the flask, by allowing a drop of water to come in contact with it, and then warming the glass until it has dissolved. On cooling it will crystallise. This is to enable the gas to be dried in the flask itself. The flask is to be filled with mercury by the aid of a small funnel reaching to the bottom. It is then to be inverted in the mercurial trough, A A. The gas, saturated with moisture, but otherwise in a state of purity, is then to be allowed to enter the flask. It is not, however, to be quite filled, but the entry of gas is to be so regulated, that the mercury in the neck shall remain a few millimetres above that in the trough. The whole is then to be allowed to remain until the gas has acquired the temperature (t) of the laboratory, at the atmospheric pressure P. The volume V of the gas, and the height p of the mercury in the flask above that in the trough, are then to be observed through the telescope of the cathetometer. The actual volume of the gas at t and P is found by consulting a previously prepared table, indicating the capacity of the flask at each of the millimetre marks on the neck. Calling the observed volume so obtained V_1, the volume V_2, at 0° C. and 760 mm. pressure, becomes:—

Fig. 755.

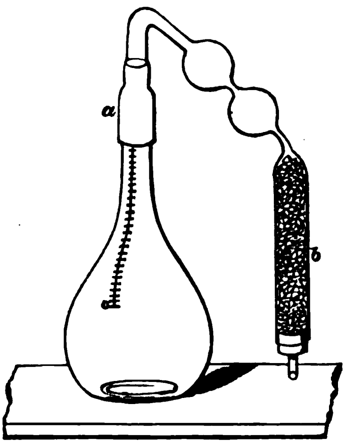


$$V_2 = \frac{V_1 (P - p)}{760 (1 + 0{\cdot}00367\, t)}.$$

The flask is then to be weighed, to obtain the weight G_2 of the corrected volume V_2.

It is necessary, in order to do this without bringing the hands in contact with the flask (which, by warming it, would alter the volume), to make use of the lever apparatus represented in the engraving at *c f*. At the end, *f*, a hollow cork is fastened containing the stopper, but it is so placed that while its superior extremity enters the flask for a short distance, it does not close it, because the wedge *d*, by raising the end *c*, keeps the end *f* depressed. When, therefore, the flask is to be closed, preparatory to the weighing, the wedge *d* is to be taken away, and the finger-plate *c*, being pressed upon the stopper, enters and closes the flask. The pin *c* is then to be withdrawn, and the flask, along with the lever *c f*, removed from the trough. The lever apparatus can then be detached from the stopper, so as to allow of the flask being placed on the pan of the balance. Previous to the weighing, it is necessary to clean the extremity of the flask with the most scrupulous care. It is to be allowed to repose on the balance until it has had time to attain the temperature t_1 of the balance-case at the pressure P_1; it may then be weighed. The number so obtained we shall call G. The glass stopper having been removed, it is to be replaced by the drying-tube *b* (*fig.* 756). It is then necessary to put the apparatus under the bell-glass of an air-pump, and exhaust and readmit the air until all the gas has been replaced by it. The stopper is again to be inserted after removal of the drying-tube, and the flask is to be reweighed. This weight is called G_1. The weight G_2 of the volume of gas V_2 measured in the flask becomes:

Fig. 756.



$$G_2 = G - G_1 + \frac{V_1 P_1}{773 \times 760 \times (1 + 0{\cdot}00367 t_1)}.$$

The number 773 is the volume in cubic centimetres of a gramme of dry air at 0°, and under a pressure of 760 millimetres in the latitude of Berlin.

The specific gravity (D) may then be found from the expression

$$D = 773 \frac{G_2}{V_2}.$$

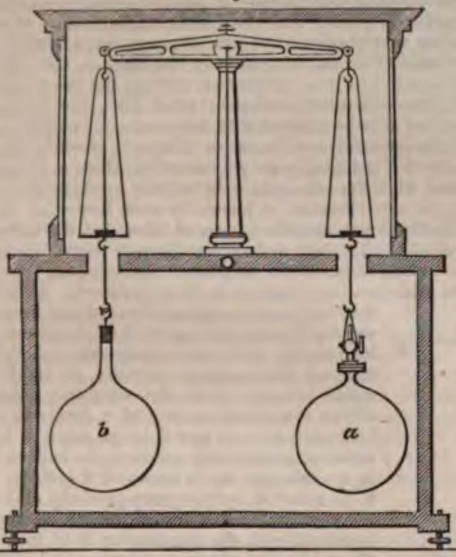
For a method of determining the specific gravity of a gas, by ascertaining the time of its effusion, as compared with the time of effusion of air, the reader is referred to Bunsen's work above cited.

Regnault's Method.

Regnault, in his magnificent work on the steam-engine above cited, gives an elaborate account of the methods employed by him to determine, with the utmost possible accuracy, the specific gravities of the more important gases. These methods are, however, far too complex, and require too elaborate apparatus to be employed in the laboratory, when, as in ninety-nine cases out of a hundred, the object in view is simply to confirm the formula of a gas which is under investigation. The process is nevertheless so perfect, and the results so trustworthy, that it would be highly improper to omit a condensed account of it.

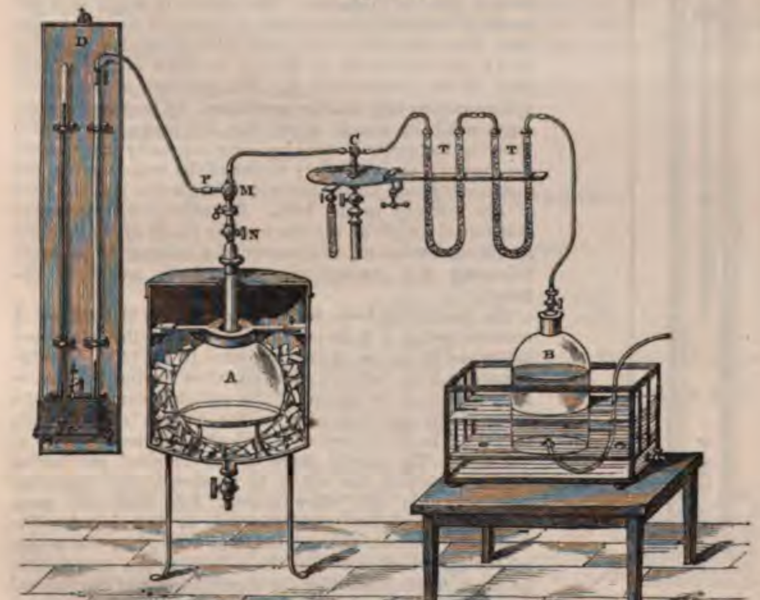
Regnault uses large balloons capable of holding ten litres. The balance, when loaded with a kilogramme in each pan, indicates readily half a milligramme. In order to do away with numerous uncertain corrections, arising from variations in the temperature, pressure, and hygrometric state of the air, the balloon in which the gases are weighed is counterpoised by another balloon of equal bulk, the same kind of glass, and of nearly equal weight. In order to determine the volume of air displaced by the balloon in which the gases are to be weighed, it is to be filled with water, and then weighed in water of the same temperature. The balloon is then to be removed and weighed, after wiping, upon a strong balance. It is plain that the difference between the two weighings is the same as the weight of water displaced by the external volume of the balloon. It is then necessary to obtain a counterpoise of precisely similar external volume, or, in other words, which displaces the same volume of air. For this purpose a balloon is selected a little smaller than the first, including its stopcock. The latter is merely closed with a cap ending in a hook, permitting it to be suspended from the balance-pan. Its volume is then ascertained, and if less than that of the balloon in which the gases are weighed, a tube closed at each end, and of a volume equal to the deficiency, is attached to it. The balloons, when adjusted, are then to be suspended beneath the scale-pans of a balance, in the manner shown in *fig.* 757.

Fig. 757.



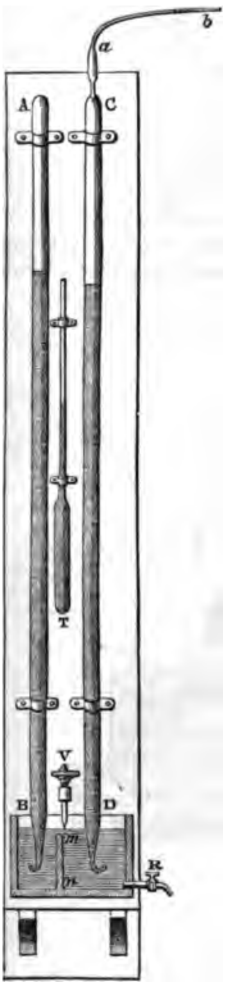
The flask, *a*, has a stopcock connected with a three-way tube, allowing it to be put in communication with a gasholder, an air-pump, and a manometric apparatus, which allows the elastic force of the gas to be ascertained with great precision. The arrangement may be seen by reference to *fig.* 758.

Fig. 758.



The stopcocks are then to be so turned as to place the balloon, A, in communication with the air-pump only, and the latter is to be worked until as perfect a vacuum as possible is obtained. The gas is then allowed to enter from the receiver B but slowly, so as to ensure its complete desiccation on passing through the tubes TT. These tubes may be charged with pumice moistened with sulphuric acid, or with fragments of chloride of calcium, or with pieces of hydrate of potassium, according to the nature of the gas. Lest any trace of air should remain in the balloon, the exhaustion and refilling are to be repeated until it is certain that nothing but the pure gas is contained in it. Before filling the exhausted globe for the last time, the sheet-iron case represented in the engraving is to be charged with fragments of ice; the taps N, M, and C then being turned, the gas is allowed to enter. When the globe is full, the tap N is to be closed. The tube at P not having as yet been slipped on, a momentary communication may be made with the atmosphere by rapidly opening and closing N. The elastic force of the gas may therefore be known by mere inspection of the barometer. The cock N being finally closed, and the system of tubes, &c. disconnected, the balloon is to be carefully wiped with a cloth sufficiently damp to prevent electrical excitation, which would cause serious errors in the weighing. The globe is then to be suspended on the balance, and after two hours' repose is to be weighed. This delay is imperative, because so large a volume of gas does not immediately acquire the temperature of the balance-case. Moreover, as long as the air of the balance-case and the balloon are of different temperatures, currents are liable to form, which would interfere with the weighings; finally, the delay allows the normal amount of moisture to condense on the balloon. As soon as weighings, taken at intervals of a few minutes, are perfectly constant, the balloon is to be replaced in the case, and again surrounded with ice. The gas is then to be removed by the pump precisely as before. In order to ascertain the elastic force of the residual gas, the tube connected with the manometer B is to be attached at P. The tube must, of course, be prevented from collapsing by a spiral of wire contained in it, or it may be made of lead. The barometric manometer is seen in section on a larger scale in *fig.* 759. The tube A B is merely a barometer of 20 mm. interior diameter. The cistern in which it is inverted is divided into two parts by means of the diaphragm *mn*. The tube CD is a glass tube of similar diameter to AB, but contracted at the top to allow of the attachment of the leaden tube *ab*. The pressure of the atmosphere may at any time be ascertained by pouring in mercury until it stands above the diaphragm, and, after lowering the screw V until its lower extremity just touches the mercury, measuring, by means of the cathetometer, the distance between the upper part of the screw and the level of the mercury in the tube. By adding the previously ascertained length of the screw to the result of the cathetometric measurement, the length of a column of mercury balancing the atmospheric pressure is accurately obtained.

Fig. 759.



The gas having been finally removed from the balloon, a communication is to be established between the latter and the tube CD, in the manner indicated in *fig.* 759. The difference in level between the two tubes having been carefully measured by means of the cathetometer, the elastic force of the gas remaining in the balloon is at once obtained. The thermometer T indicates the temperature at the time. The elastic force of the residual gas having been ascertained, the tap is to be closed, the connecting tube removed; and after wiping, &c., with the same precautions as before, the balloon is to be weighed. The difference between the weighings $(P-p)$ gives the weight of the gas which at 0° fills the balloon at the atmospheric pressure H, diminished by the elastic force, h, of the residual gas. The weight of the gas at the normal temperature and pressure then becomes:

$$(P-p)\frac{760}{H-h}$$

SPECIFIC GRAVITIES OF VAPOURS, OR VAPOUR-DENSITIES.

The determination of the vapour-density of a substance being the most severe check that can be obtained on the results of analysis, it necessarily becomes a process of constant occurrence in laboratories of research. All substances that volatilise without decomposition, at temperatures that can be accurately measured, can have their atomic weights determined in this manner, but the process to be employed will depend upon a number of variable conditions.

It is not intended in this article to describe all the processes which have been devised at various times to meet special cases, but it will be proper to consider those which have been found of general applicability and sufficient accuracy.

There are certain precautions which must be observed in *all* cases where the vapour-density of a substance is to be determined; these will be described in the first instance.

General precautions to be observed previous to determining Vapour-densities.—1. It is essential that the substance be entirely volatile without decomposition. It sometimes happens that the substance, although possessing this first and most essential quality, is nevertheless so readily oxidisable, that it cannot be distilled in a vessel containing air or oxygen without forming oxidised products, which are comparatively fixed. It is easy in most cases to overcome this difficulty, by filling the balloon with hydrogen previous to employing the method of Dumas, presently to be described. It even happens, at times, that the substance is (like isoprene), so readily oxidisable at ordinary temperatures, that, even when the vapour-density is determined by a process which does not allow of its coming in contact with air or oxygen at a high temperature, a portion of the substance is unable to assume the gaseous form. This may generally be avoided by preparing the substance only a short time before the operation, or by rectifying it over sodium immediately previous to inserting it into the bulb or tube, presently to be described.

2. It is very important that the substance shall be entirely free from bodies of higher or lower boiling-point. In the first case, the density will generally come out too high, and in the second too low. If, therefore, the substance to be experimented on be one of an homologous series, and be contaminated with any of its congeners, it is absolutely necessary that it be subjected to an elaborate fractional distillation, or other method of purification, before being examined.

3. The substance must be perfectly dry. It is obvious that the presence of comparatively small portions of water will lower the density of most organic vapours to an extent sufficient to destroy all confidence in the result as a means of checking a formula.

There are a few more precautions, of a somewhat less general character, but they will be considered in describing the various processes.

The methods which we shall describe are the following:

1. The process of Gay-Lussac.
2. „ „ Dumas.
3. „ „ H. Ste-Claire Deville and Troost.
4. „ „ Regnault.

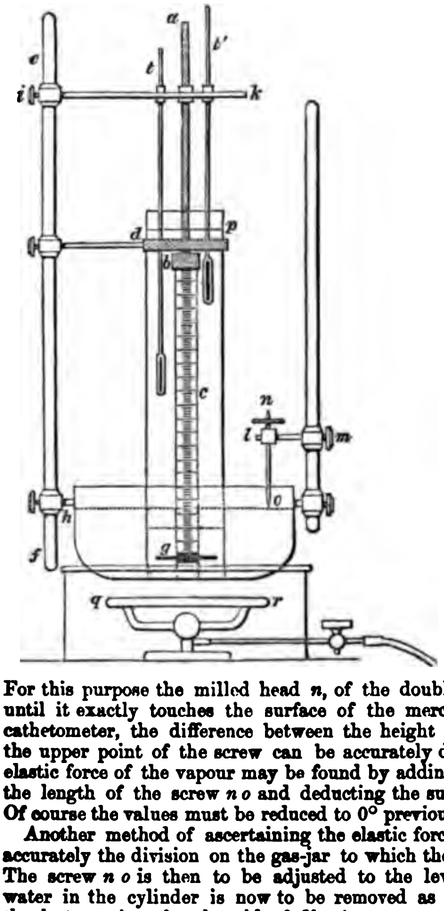
We shall also incidentally consider the following special cases:—

a. The substance is liquid, and boils below 100°.
b. „ „ „ „ above 100°, but below 150°.
c. „ „ „ „ above 150°, but below 300°.
d. „ „ solid, and boils below 300°.
e. „ „ liquid or a fusible solid, and boils above 300°, but below 350°.
f. „ „ boils above 350°, but below 440°.
g. „ „ „ above 440°, but below 860°.
h. „ „ „ above 860°, but below 1040°.

1. *The process of* Gay-Lussac.

a. The substance is liquid, and boils below 100°.—This simple and beautiful process consists in ascertaining the volume (V) occupied by a given weight (W) of a substance when heated to the temperature T, at a known pressure P. For this purpose a small iron pan is to be supported over a charcoal furnace or a powerful gas-lamp. A glass gas-jar (*c*) divided into cubic centimetres is, after drying, to be filled with mercury, and inverted in the trough. A small glass bulb, containing a known weight of the liquid, is then to be passed up into the gas-jar. It is of great importance that this bulb should be as thin as possible, so that it may not fail to burst by the mere expansion of the liquid. For this purpose it is also necessary that the bulb be perfectly filled. A large glass cylinder open at both ends is then to be lowered over the gas-jar. The gas-jar may be kept in the axis of the cylinder by means of the metal piece *g* having three projections, and also by means of the rod *a b*, carrying a cap *b*. The rod *a b* passes through one of three apertures in the arm *i k*, which slides on the upright rod *e f*, attached to the iron pot at *h*. The arm *i k* also allows two thermometers, *t* and *t′*, to be supported by means of pierced corks at different heights in the cylinder. The arm *l m* supports a double-pointed screw of known length, the use of which will be described presently. The cylinder is now to be filled with water up to the line *d p*, and heat is to be applied by means of the circular burner, *q r*. The liquid in the cylinder will now gradually increase in temperature, and at a certain point the bulb will burst, and the mercury will begin slowly to descend in the gas-jar. Soon after the water enters into ebullition, it will be found that the vapour will cease to expand any further. The volume *V* may then be noted, as also the temperature *T*, and the height of the barometer. But to obtain the true elastic force, *P*, of the vapour, it will be necessary to ascertain the height of the mercury in the jar above that in the trough, and to deduct this value from the height of the barometer. For this purpose the milled head *n*, of the double pointed screw *n o*, is to be turned until it exactly touches the surface of the mercury in the trough. By means of a cathetometer, the difference between the height of the mercury in the gas-jar and the upper point of the screw can be accurately determined. It is obvious that the elastic force of the vapour may be found by adding to the reading of the cathetometer the length of the screw *n o* and deducting the sum from the height of the barometer. Of course the values must be reduced to 0° previous to calculating the results.

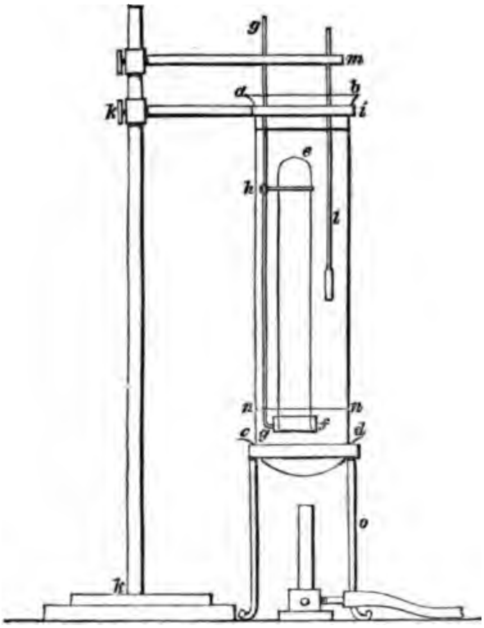
Fig. 760.



Another method of ascertaining the elastic force of the vapour is as follows. Note accurately the division on the gas-jar to which the inner level of the mercury reaches. The screw *n o* is then to be adjusted to the level of the mercury in the pot. The water in the cylinder is now to be removed as far as possible with a siphon, and the last portions by the aid of filtering-paper. The metal will then, of course, be found to have receded from the point of the screw. More metal is now to be added, until it exactly touches the point of the screw again. The exact point to which this level reaches on the gas-jar is to be noted. The distance between these two points, being deducted from the height of the barometer, gives the elastic force *P* of the vapour at the temperature *T*.

A more generally convenient form of apparatus for determining vapour-densities by Gay-Lussac's method, and one which requires a much smaller quantity of mercury, is represented in fig. 761. It consists of a cylinder of rather thin glass, *a b c d*, in shape like a very large test-tube; it may be about 16 or 18 inches long, and 5 or 6 in diameter. At the lower and closed end it is rounded, and care must be taken that it is thin enough to stand the application of heat, and yet strong enough to bear the weight of the mercury and the rest of the apparatus which will have to be inserted. A small and rather light gas-jar *e*, divided into half cubic centimetres, is supported at its lower end by an iron cup *f*, attached to a rod *g g* of the same metal. In the engraving it is represented in the act of being lowered into its place. The upper end of the jar is kept steady by the ring *h* which slides on the rod *g g*. The cylinder is retained in its vertical position by the ring *i* sliding on the massive retort-stand *k k*. The rod *g g* and the thermometer *l* are supported by the arm *m*, also attached to the retort-stand. The cylinder being charged up to the line *n n* with mercury, the gas-jar, filled with mercury, and having the glass bulb containing the fluid to be examined inserted, is placed in the position seen in the figure. The cylinder is then to be filled with water, or neat's-foot oil, until the gas-jar is covered for at least an inch. The cylinder may be supported on wire-gauze over the tripod *o*, or in any other convenient manner. Heat may be applied by means of a Bunsen's burner.

Fig. 761.



Great care must be taken, in passing the bulb up into the gas-jar, to prevent fracture. The most convenient way of accomplishing this, is to place the lower end of the jar in a mercurial trough, and to incline it to an angle of about 45°. The bulb is then to be held between the thumb and two first fingers, the tail towards the palm of the hand; it is then to be presented to the opening of the gas-jar, and when inserted is to be let go; it will then ascend to the top.

The elastic force of the gas can be very readily determined, owing to the transparency of the cylinder. With this apparatus the height of the column of oil or water must be ascertained, and reduced by calculation to a corresponding value in millimetres of mercury. The elastic force of the vapour is then found by adding this number to the height of the barometer, and deducting the height of the mercury in the gas-jar above the level of the mercury in the outer cylinder.

By proceeding according to either of the methods described, we ascertain the volume which a known weight of substance occupies at a given temperature and pressure, and it only remains to determine the weight *W* of the same volume *V* of air at the same temperature *T* and pressure *P*. This may be ascertained by means of the following formula:

$$W = 0{\cdot}0012932 \text{ grm} . V . \frac{1}{1 + 0{\cdot}00367\,T} . \frac{P}{760}$$

The expression $1 + 0{\cdot}00367\,T$ for the temperatures at which the specific gravities of *gases* are usually determined, has been calculated by several physicists, and may be found in works on physics; and an especially elaborate table of this description, for every tenth of a degree between − 2° and + 40°, may be found in Roscoe's translation of Bunsen's *Gasometry*. But it is evident that vapour-densities are almost always determined at temperatures more elevated than this: the author of this article has, therefore, calculated the more comprehensive expression $\frac{1}{1 + 0{\cdot}00367\,T}$ for all the temperatures at which a vapour-density is likely to be determined by Gay-Lussac's process—viz., from 1° to 150°. This table will, from the time which it will save in calculating, be found invaluable to those who have many determinations of this class to make.

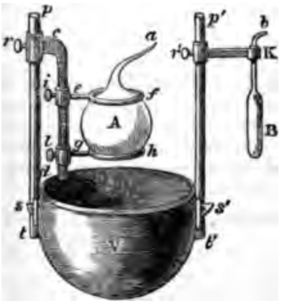
b. The substance is liquid, and boils above 100°, *but below* 150°.—The process of Gay-Lussac is quite capable of meeting this case, but, instead of water, it will be necessary to substitute neat's-foot oil, or spermaceti. During the operation the oil must be stirred by the aid of a small stirrer attached to a wire. As oil does not remain colourless if heated for a long time to 150°, it is advisable to make the experiment in such a position, that a good light from a window or lamp may be brought behind it, so as to illuminate the divisions on the gas-jar and thermometer. In other respects the operation may be conducted in the same manner as that last described.

Table for the Calculation of $\frac{1}{1 + 0{\cdot}00367\,T}$

T.		T.		T.		T.		T.	
1	0·99634	31	0·89785	61	0·81708	91	0·74964	121	0·69249
2	0·99271	32	0·89490	62	0·81464	92	0·74758	122	0·69073
3	0·98911	33	0·89197	63	0·81221	93	0·74554	123	0·68899
4	0·98553	34	0·88906	64	0·80979	94	0·74351	124	0·68725
5	0·98198	35	0·88617	65	0·80740	95	0·74148	125	0·68552
6	0·97845	36	0·88330	66	0·80501	96	0·73947	126	0·68380
7	0·97495	37	0·88044	67	0·80264	97	0·73747	127	0·68209
8	0·97148	38	0·87761	68	0·80028	98	0·73548	128	0·68038
9	0·96803	39	0·87479	69	0·79794	99	0·73350	129	0·67869
10	0·96460	40	0·87199	70	0·79561	100	0·73153	130	0·67700
11	0·96120	41	0·86921	71	0·79329	101	0·72957	131	0·67532
12	0·95782	42	0·86645	72	0·79099	102	0·72762	132	0·67365
13	0·95446	43	0·86370	73	0·78870	103	0·72568	133	0·67199
14	0·95113	44	0·86097	74	0·78642	104	0·72376	134	0·67034
15	0·94782	45	0·85826	75	0·78416	105	0·72184	135	0·66870
16	0·94454	46	0·85556	76	0·78191	106	0·71993	136	0·66706
17	0·94127	47	0·85289	77	0·77967	107	0·71803	137	0·66543
18	0·93803	48	0·85022	78	0·77745	108	0·71615	138	0·66380
19	0·93482	49	0·84758	79	0·77523	109	0·71427	139	0·66219
20	0·93162	50	0·84495	80	0·77304	110	0·71240	140	0·66059
21	0·92844	51	0·84234	81	0·77085	111	0·71055	141	0·65899
22	0·92529	52	0·83974	82	0·76867	112	0·70870	142	0·65740
23	0·92216	53	0·83716	83	0·76651	113	0·70686	143	0·65582
24	0·91905	54	0·83460	84	0·76436	114	0·70503	144	0·65424
25	0·91596	55	0·83205	85	0·76222	115	0·70321	145	0·65268
26	0·91289	56	0·82952	86	0·76010	116	0·70140	146	0·65112
27	0·90984	57	0·82700	87	0·75798	117	0·69960	147	0·64957
28	0·90682	58	0·82450	88	0·75588	118	0·69781	148	0·64802
29	0·90381	59	0·82201	89	0·75379	119	0·69603	149	0·64648
30	0·90082	60	0·81954	90	0·75171	120	0·69425	150	0·64495

2. *The process of* Dumas.

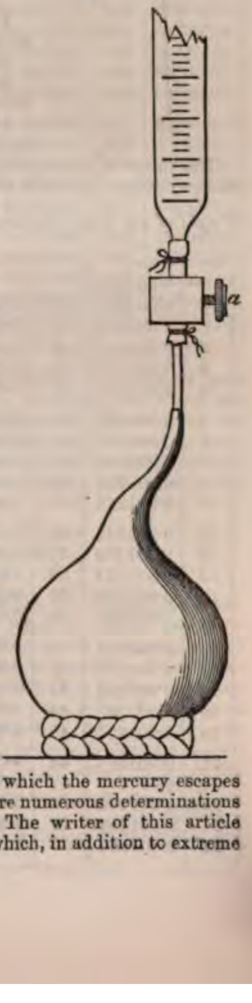
Fig. 762.



c. The substance is liquid, and boils above 150°, *but below* 300°.—The process best adapted for determining the vapour-densities of liquids boiling between the above temperatures is that of Dumas. For this purpose it is proper to employ glass balloons, having a capacity of from 100 to 350 cubic centimetres; the size will depend, to a great extent, upon the quantity of substance at the disposal of the operator. It is, however, absolutely necessary to have more substance than is sufficient to fill the balloon with its vapour. It is also proper to use larger balloons as the density of the vapour is lower; otherwise the difference between the weight of the balloon filled with vapour, and when filled with air, will be so small as to render excessively accurate weighing necessary, in order to prevent error. Dumas' method of determining vapour-densities is quite capable of yielding accurate results in the cases *a* and *b*; but it requires more substance, and does not permit of the density being determined at more than one temperature, without making a separate experiment in each case. The process of Gay-Lussac, on the other hand, permits numerous experiments with one small specimen of substance at any desired temperature within certain ranges, and thus enables the operator, in a very short time, to accumulate information regarding certain physical properties of substances which it is often very desirable to know—such, for example, as the lowest temperature at which the substance under study begins to obey the laws of permanent gases.

The balloons should be selected of a light and readily fusible glass, so as to allow the point to be sealed hermetically without difficulty at the close of the operation. One having been selected, and its neck having been drawn out to a moderately fine point, it is to be thoroughly dried. This may be done by exhausting it repeatedly, and allowing it to fill each time with air dried by passing over a column of chloride of calcium. The balloon is then to be weighed, the same precautions being taken as in the case of gases. As much fluid is then to be inserted as it is judged will be more than enough to fill it with vapour. An iron pot V (*fig.* 762), having been filled with melted tallow or neat's-foot oil, is to be supported in any convenient way over a charcoal furnace, or a powerful gas-burner. For all ordinary experiments, the air-thermometer b B may be replaced by a mercurial one passing through a cork at K. The ears s and s' of the pot V support two rods, $t\,p$ and $t'\,p'$. The former has sliding upon it a bent arm, $c\,d$, capable of being fixed at any height by the screw r. Two rings, $e\,f$ and $g\,h$, serve to support the balloon A; they may be adjusted by the screws $i\,l$. The tallow being heated to nearly the boiling-point of the substance, the balloon is to be lowered gradually, until the point a projects only about half or three-quarters of an inch above the tallow. When the temperature reaches the boiling-point, the vapour begins to escape, rapidly at first, but more and more gently afterwards, and finally ceases. The absolute cessation of the evolution of the vapour may be ascertained by bringing a piece of cold metal near the point a. The liquid which condenses in the neck is to be chased away with a piece of red-hot charcoal. The temperature should be allowed gradually to rise, until it is 20 or 30 degrees above the boiling-point of the substance. The heat must then be so regulated as to allow the bath to remain as nearly as possible at the same temperature, while the point of the balloon is being sealed. This latter operation is most conveniently effected by the aid of a Herapath's blowpipe, attached to a flexible tube of sufficient length to allow of ample freedom of movement. A common mouth-blowpipe and spirit-lamp will suffice when the gas-apparatus is not at hand.

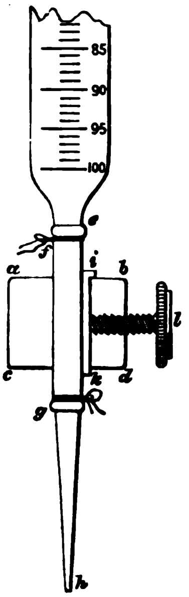
Fig. 763.



As soon as it is deemed that the point is perfectly closed, the temperature of the bath and the height of the barometer are to be noticed; the screw r may then be loosened, and the balloon raised completely from the bath; the point a should then be turned downwards, so that the condensed liquid may flow into it. It should now be carefully watched, to see if any air-bubbles rise through it, indicating incomplete sealing. If no leak be observed, the balloon may, after cooling, be thoroughly cleaned, placed on the balance-pan, and allowed to remain long enough to become constant in weight. The exact weight having been ascertained, the point a is to be inserted below the surface of the metal in the mercurial trough, and a file-mark having been made on it, the point is to be snapped off. The mercury will then rush in, and, if the operation has been completely successful, will, with the condensed liquid, entirely fill the balloon. In most cases, however, a bubble of air will remain, indicating that the whole has not been expelled from the balloon by the vapour. It is absolutely essential that the volume of this residual air should be accurately ascertained. For this purpose the mercury and condensed liquid are to be transferred to a cylinder, divided into cubic centimetres, and placed in a vertical position. A mirror then being held behind the cylinder, and in contact with it, the operator places himself in such a position that the line on the cylinder which coincides with the level of the mercury, or rather that of the condensed liquid, also coincides with the centre of the reflection of the pupil of the eye as seen in the mirror. The balloon is then to be refilled entirely with mercury, and the contents are to be again transferred to the graduated cylinder, and the volume ascertained as before. It is obvious that the second reading will give a greater value than the first, and that the difference between the two readings will indicate the volume of the residual air.

The above process for the determination of the residual air takes a considerable time, owing to the slowness with which the mercury escapes from the small aperture in the neck of the balloon, and, where numerous determinations of vapour-density have to be made, causes great delay. The writer of this article has therefore devised the following method of proceeding, which, in addition to extreme simplicity and accuracy, has the advantage of occupying only a few seconds (Phil. Trans. 1857, p. 460). The point of the balloon having been broken off under mercury, and the metal having entered the globe, the latter is to be placed on a straw ring (as in *fig.* 763, p. 369), beneath a burette divided into cubic centimetres and fractions. The screw *a* of the compression-stopcock is then turned, so as to allow a slow stream of metal to flow into the balloon until the condensed liquid exactly reaches the orifice. The quantity of mercury required for the purpose at once indicates the residual air. The compression-stopcock shown in *fig.* 763 is seen in section in *fig.* 764. It is capable of withstanding a very considerable pressure of mercury, and is so manageable that the smallest portion can be added at will. A block of wood, *a b c d*, has a square hole mortised in it, through which passes the vulcanised tube *e f g k*, attached at *e f* to the lower orifice of the burette. A piece of hard wood, *i k*, also passes through the mortise, and is retained in its place by the flange *i*. To close the orifice it is only necessary to turn the milled head *l* of the screw; the piece *i* will then be pressed against the vulcanised tube, and close it.

Fig. 764.



From the data obtained in an experiment conducted as above, the vapour-density (D) may be calculated in a few minutes with sufficient accuracy for most purposes, by the aid of the following formula:—

$$D = \frac{P + Vn_t}{(V - v)n_t'}$$

P = the difference in weight between the globe filled with air and when filled with vapour.

V = the capacity of the balloon in cubic centimetres.

n_t = the weight of one cubic centimetre of air at the temperature at which the balloon filled with air was weighed.

n_t' = the weight of one cubic centimetre of air at the temperature of sealing the globe.

The values of n_t and n_t' (in grammes) may be obtained at once from the following table, calculated for each degree centigrade from 0° to 300°:—

Weight of one Cubic Centimetre of Atmospheric Air at different Temperatures, from 0° *to* 300° *at* 760 *mm.*

0°	0·001293								
1	0·001288	26°	0·001181	51°	0·001091	76°	0·001011	101°	0·000943
2	0·001284	27	0·001177	52	0·001088	77	0·001008	102	0·000941
3	0·001279	28	0·001173	53	0·001084	78	0·001005	103	0·000938
4	0·001275	29	0·001169	54	0·001081	79	0·001002	104	0·000936
5	0·001270	30	0·001165	55	0·001077	80	0·001000	105	0·000933
6	0·001266	31	0·001161	56	0·001074	81	0·000997	106	0·000931
7	0·001261	32	0·001157	57	0·001070	82	0·000994	107	0·000928
8	0·001257	33	0·001154	58	0·001067	83	0·000992	108	0·000926
9	0·001252	34	0·001150	59	0·001063	84	0 000989	109	0·000923
10	0·001248	35	0·001146	60	0·001060	85	0·000986	110	0·000921
11	0·001243	36	0·001142	61	0·001057	86	0·000983	111	0·000919
12	0·001239	37	0·001138	62	0·001053	87	0·000980	112	0·000916
13	0·001234	38	0·001134	63	0·001050	88	0·000977	113	0·000914
14	0·001230	39	0·001131	64	0·001047	89	0·000974	114	0·000911
15	0·001225	40	0·001128	65	0·001044	90	0·000972	115	0·000909
16	0·001221	41	0·001124	66	0·001041	91	0·000969	116	0·000907
17	0·001217	42	0·001121	67	0·001038	92	0·000967	117	0·000905
18	0·001213	43	0·001118	68	0·001035	93	0·000964	118	0·000903
19	0·001209	44	0·001114	69	0·001032	94	0·000962	119	0·000900
20	0·001205	45	0·001111	70	0·001029	95	0·000959	120	0·000898
21	0·001201	46	0·001108	71	0·001026	96	0·000956	121	0·000896
22	0·001197	47	0·001105	72	0·001023	97	0·000953	122	0·000894
23	0·001193	48	0·001102	73	0·001020	98	0·000951	123	0·000891
24	0·001189	49	0·001098	74	0·001017	99	0·000948	124	0·000889
25	0·001185	50	0·001095	75	0·001014	100	0·000946	125	0·000887

Weight of one Cubic Centimetre of Atmospheric Air at different Temperatures, from 0° *to* 300° *at* 760 *mm.* (continued.)

126	0·000884	161	0·000813	196	0·000752	231	0·000699	266	0·000654
127	0·000882	162	0·000811	197	0·000751	232	0·000698	267	0·000653
128	0·000880	163	0·000809	198	0·000749	233	0·000697	268	0·000652
129	0·000878	164	0·000807	199	0·000748	234	0·000695	269	0·000651
130	0·000876	165	0·000806	200	0·000746	235	0·000694	270	0·000650
131	0·000874	166	0·000804	201	0·000744	236	0·000692	271	0·000648
132	0·000871	167	0·000802	202	0·000743	237	0·000691	272	0·000647
133	0·000869	168	0·000800	203	0·000740	238	0·000690	273	0·000646
134	0·000867	169	0·000798	204	0·000739	239	0·000689	274	0·000645
135	0·000865	170	0·000796	205	0·000737	240	0·000688	275	0·000643
136	0·000863	171	0·000794	206	0·000736	241	0·000686	276	0·000642
137	0·000860	172	0·000793	207	0·000734	242	0·000685	277	0·000641
138	0·000858	173	0·000791	208	0·000733	243	0·000683	278	0·000640
139	0·000856	174	0·000789	209	0·000731	244	0·000682	279	0·000639
140	0·000854	175	0·000788	210	0·000730	245	0·000681	280	0·000638
141	0·000852	176	0·000786	211	0·000728	246	0·000679	281	0·000636
142	0·000850	177	0·000784	212	0·000727	247	0·000678	282	0·000635
143	0·000848	178	0·000782	213	0·000725	248	0·000677	283	0·000634
144	0·000846	179	0·000781	214	0·000724	249	0·000675	284	0·000633
145	0·000844	180	0·000779	215	0·000722	250	0·000674	285	0·000631
146	0·000842	181	0·000777	216	0·000721	251	0·000673	286	0·000630
147	0·000840	182	0·000776	217	0·000719	252	0·000672	287	0·000629
148	0·000838	183	0·000774	218	0·000718	253	0·000670	288	0·000628
149	0·000836	184	0·000772	219	0·000716	254	0·000669	289	0·000627
150	0·000834	185	0·000770	220	0·000715	255	0·000668	290	0·000626
151	0·000832	186	0·000769	221	0·000713	256	0·000666	291	0·000625
152	0·000830	187	0·000767	222	0·000712	257	0·000665	292	0·000624
153	0·000828	188	0·000765	223	0·000710	258	0·000664	293	0·000623
154	0·000826	189	0·000763	224	0·000709	259	0·000663	294	0·000622
155	0·000824	190	0·000762	225	0·000708	260	0·000662	295	0·000621
156	0·000822	191	0·000760	226	0·000706	261	0·000660	296	0·000620
157	0·000821	192	0·000758	227	0·000705	262	0·000659	297	0·000619
158	0·000819	193	0·000757	228	0·000703	263	0·000658	298	0·000618
159	0·000817	194	0·000755	229	0·000702	264	0·000657	299	0·000617
160	0·000815	195	0·000754	230	0·000701	265	0·000655	300	0·000616

But the formula last given does not afford results of sufficient exactness for very delicate experiments, inasmuch as it does not include some necessary corrections, the most important being one for the expansion of glass. Regnault's formula, on the other hand, includes all the corrections required, and possesses also the merit of simplicity. The weight P of the balloon having been ascertained, and the temperature t of the balance-case, and the height (H) of the barometer having been noted, it is evident that the weight, p, of the air in the balloon will be:

$$p = 0{\cdot}0012932\, V \cdot \frac{1}{1 + 0{\cdot}00367\, t} \cdot \frac{H}{760};$$

V being the capacity of the balloon in cubic centimetres.

The point of the balloon having been sealed, and the height, H', of the barometer, and the apparent temperature, T, of the bath having been taken, it will be necessary to find the true temperature, T', which corresponds to it. It must be remembered that only a small portion of the tube of the thermometer is heated in the bath. It is therefore proper to have a small thermometer so placed that its bulb is in contact with the tube of the principal thermometer, and at the height of about one-half of that portion of the mercurial column which projects above the oil or tallow of the bath, and the division θ of the principal thermometer, which should be two or three centimetres above the bath. It may then be admitted that $(T-\theta)$ represents the portion of the mercurial column at the average temperature t. This portion would dilate by $(T-\theta) \cdot \frac{T-t}{6380}$ if heated from t to T. The true temperature T' is therefore found by adding to the apparent temperature, T, the number of degrees indicated by the expression $(T-\theta)\frac{T-t}{6380}$. But the temperature T', as indicated by a mercurial thermometer, must be exchanged for the corresponding temperature T'', as indicated by an air-thermometer; this may be obtained without experiment from the following table, founded on the experiments of Regnault:—

Table for the Conversion of the Degrees (T') of a Mercurial Thermometer into the corresponding Values (T'') of an Air Thermometer.

T'.	T''.	T'.	T''.	T'.	T''.	T'.	T''.
100°	100°	169·68	170	239·90	240	301·08	300
109·98	110	179·63	180	250·05	250	311·45	310
119·95	120	189·65	190	260·20	260	321·80	320
129·91	130	199·70	200	270·38	270	332·40	330
139·85	140	209·75	210	280·52	280	343·00	340
149·80	150	219·80	220	290·80	290	354·00	350
159·74	160	229·85	230				

The balloon having been sealed, and well cleaned, its weight (P') is to be determined; the weight of the vapour will therefore be $P'-(P-p)$.

The residual air, v, having been found in the usual manner, and the temperature t'' and pressure H'' noted, its weight p' may be ascertained by means of the expression:

$$p' = 0{\cdot}0012932 \text{ grm} . v \frac{1}{1 + 0{\cdot}00367t''} . \frac{H''}{760}$$

The weight of the vapour becomes, therefore, $(P'-P + p-p')$.

But it is evident that to obtain the true volume of the vapour we must deduct the volume of the residual air at the temperature of sealing the balloon, which, even as corrected, we shall for simplicity's sake call T. The volume v' of the residual air at T and H' will be:

$$v' = v \frac{1 + 0{\cdot}00367 . T}{1 + 0{\cdot}00367 . t''} . \frac{H''}{H'}.$$

Calling the coefficient of expansion of glass k, we have for the volume of the vapour at T and H' $[V(1 + kT) - v']$. The density of the vapour will therefore be:

$$\frac{P' - P + p - p'}{0{\cdot}0012932[V(1 + kT) - v'] \frac{1}{1 + 0{\cdot}00367 . T} . \frac{H'}{760}}.$$

or, at full length:

$$\frac{P' - P + \left(\frac{0{\cdot}0012932}{760(1 + 0{\cdot}00367t)}(V - v)H\right)}{\left[V(1 + kT) - v\frac{1 + 0{\cdot}00367T}{1 + 0{\cdot}00367t}\right]\frac{0{\cdot}0012932}{760(1 + 0{\cdot}00367T)} . H'}.$$

For very full details regarding the calculations in vapour-density determinations, see Brown (Chem. Soc. J. [2], iv. 72).

As the expression $\frac{1}{1 + 0{\cdot}00367 . T}$ can be taken at once from the table given under section *b*, the calculation is by no means a long one.

If the height (H') of the barometer has been taken in inches, it can be reduced at once to millimetres from the following table, extracted from the writer's *Handbook of Chemical Manipulation*:—

Table for the Conversion of Inches into Millimetres.

Inches.	Millimetres.	Inches.	Millimetres.
1	25·39954	6	152·3972
2	50·79908	7	177·7968
3	76·19862	8	203·1963
4	101·5982	9	228·5959
5	126·9977		

The coefficient of expansion of glass may be ascertained, for temperatures between 0° and 350°, by inspection of the following table (**Regnault**):—

Between 0° and 100°	K = 0·0000276
„ 150	0·0000284
„ 200	0·0000291
„ 250	0·0000298
„ 300	0·0000306
„ 350	0·0000313

In laboratories where vapour-densities are frequently being determined, it will be found of great advantage to keep copies, not only of all the data obtained in such experiments as the above, but also of each step in the calculations; so that, in the event of real or supposed error, the point at which it has occurred can be detected at once.

When the quantity of the residual air is small, and the atmospheric pressure is not far from 760 mm., its weight may be obtained with sufficient accuracy by multiplying the number opposite the temperature in the table on p. 370 by the number of cubic centimetres found.

d. The substance is solid, and boils below 300°.—The last-described method is quite capable of meeting the case, it being only necessary to fuse the substance so as to allow of its being inserted in the balloon.

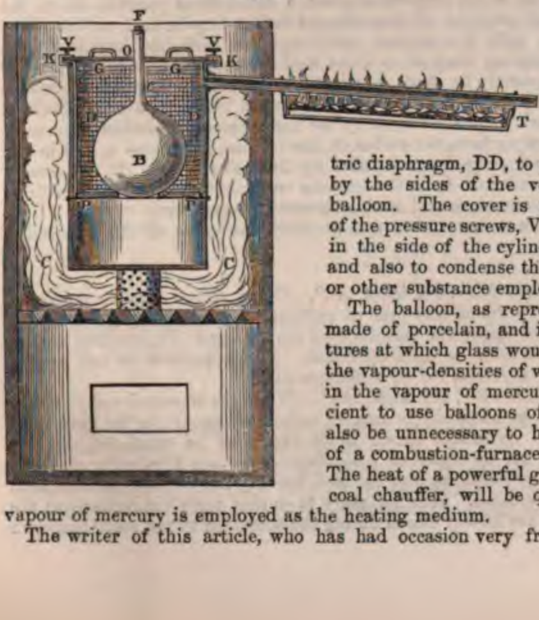
3. *The process of* **Deville** *and* **Troost**.

e. The substance is fluid or a fusible solid, and boils above 300°, *but below* 350°.—The chief difficulty in determining the vapour-densities of substances boiling beyond the range of the mercurial thermometer has been the accurate determination of the temperature. MM. **Deville** and **Troost** (Ann. Chim. Phys. [3], lviii. 257) have most ingeniously and successfully overcome this difficulty, by heating the balloons in the vapour of substances of elevated, but accurately known, boiling-points. It is evident that with homogeneous substances the temperature of their vapours, in contact with the boiling substances, is invariable as long as the pressure remains constant. Thus, under these circumstances, a thermometer surrounded by steam escaping from boiling water, will always indicate 100°. The same phenomena present themselves with bodies requiring much higher temperatures for vaporisation; the substances most convenient for the purpose are mercury boiling at 350°, sulphur at 440°, cadmium at 860°, and zinc at 1040°. In the case now under consideration, it is sufficient to use mercury the boiling-point of which is 350°.

The apparatus required is of the simplest description. It consists of an iron cylinder, CCKK (*fig.* 765), 22 centimetres high and 12 centimetres in diameter. It may very conveniently be constructed out of a mercury-bottle. It is to be closed with an iron cover, GG, pierced in its centre to allow of the passage of the neck of the balloon, B. The latter rests upon a ring of metal, PP, supported on points fixed to the interior of the cylinder. There is also a concentric diaphragm, DD, to prevent the heat radiated by the sides of the vessel from reaching the balloon. The cover is fastened down by means of the pressure screws, VV. The tube, T, inserted in the side of the cylinder, serves to carry away and also to condense the vapour of the mercury or other substance employed.

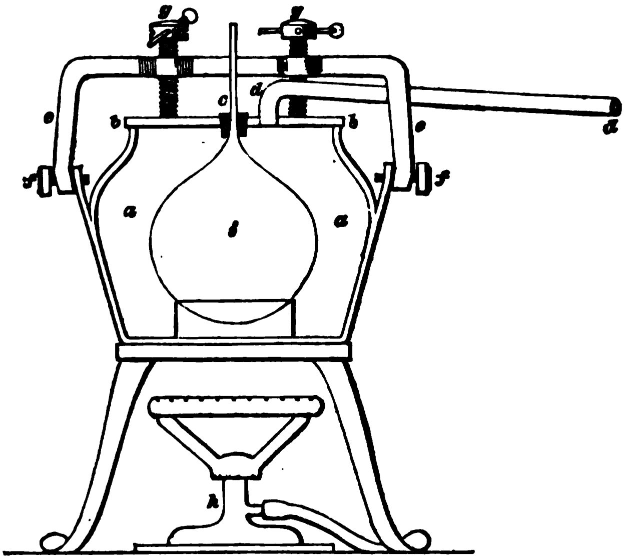
The balloon, as represented in the figure, is made of porcelain, and is used only for temperatures at which glass would soften: for substances the vapour-densities of which can be determined in the vapour of mercury, it will be quite sufficient to use balloons of ordinary glass. It will also be unnecessary to heat the tube T by means of a combustion-furnace, as shown in the figure. The heat of a powerful gas-burner, or small charcoal chauffer, will be quite sufficient when the vapour of mercury is employed as the heating medium.

Fig. 765.



The writer of this article, who has had occasion very frequently to employ this process, makes use of the apparatus shown in *fig.* 766. A small glue-pot, *a a*, is to be ground at its mouth, to fit accurately the iron plate *b b*. The latter is pierced with two holes—one serving to give egress to the neck *c* of the balloon, and the other to admit the bent iron tube *d d*, which serves to carry away and condense the vapour of the mercury. The gland *e e*, bent twice at right angles, has two screws *f f*, which attach it to the ears of the pot. The gland is pierced with three holes, two serving to admit the pressure-screws *g g*, and one to permit the passage of the neck of the balloon. A ring gas-burner (*h*) serves to heat the apparatus. The substance to be examined having been inserted in the balloon, *i*, and a few pounds of mercury having been placed in the pot, the balloon is to be put in its place, the neck passing through a cork, the upper portion of which projects as short a distance as possible above the cover of the pot. A small quantity of linseed-meal luting may be laid on the cover before fastening it down with the screws. Although the cork and luting will be destroyed during the operation, they serve quite well for one experiment. Another iron tube may very conveniently be made to slip over the tube *d d*, so as to conduct the condensed mercury-vapour to a convenient receptacle. The neck of the balloon must be kept very hot during the operation, by the aid of pieces of red-hot charcoal. When no more vapour escapes from the orifice of the balloon, it is to be sealed in the same manner as in vapour-density determinations by Dumas's method. It is scarcely necessary to add that the value of *k*, in the formula on p. 372, is too considerable to be neglected in determinations conducted at this elevated temperature.

Fig. 766.



It will save some trouble to remember that at 350° the value of the expression $\frac{1}{1+0\cdot00367\,T}$ is 0·000566.

f. The substance boils above 350°, *but below* 440°.—Glass globes may be employed for a temperature of 440° without any fear of softening. 500 or 600 grammes of sulphur are to be used in the apparatus described on pp. 373 and 374, and 200 or 300 grammes are to be distilled over in each operation. The apparatus is not injured by the sulphur, and lasts, therefore, for an indefinite time.

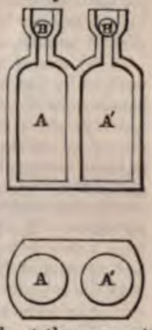
g. The substance boils above 440°, *but below* 860°.—When the vapour-density is to be determined at 860°, it will be necessary to employ cadmium-vapour for the purpose of heating the balloon. The apparatus shown in *fig.* 765 must be employed, and the tube *T* must be kept very hot by means of a combustion-furnace filled with charcoal. Two or three kilogrammes of cadmium may be used, but only 300 or 400 grammes need be distilled over in each operation. It is necessary to employ porcelain balloons at the temperature of 860°; they are loosely closed during the operation by the small porcelain stopper F (*fig.* 765, p. 373), which permits the escape of the vapour of the substance under examination. The opening is closed at the end of the experiment, by directing the flame of the oxyhydrogen-blowpipe over the stopper; the opening then closes without difficulty. For details as to the numerous precautions to be observed and corrections to be made in calculating the results, the reader is referred to the elaborate paper of MM. Deville and Troost, previously alluded to. It may be mentioned, however, that the coefficient of cubic dilatation of porcelain between 0° and 860° was found by the authors to be 0·0000108.

h. The substance boils above 860°, *but below* 1040°.—In this case it will be necessary to employ the vapour of zinc. The general process is similar to that employed in the case of cadmium. The coefficient of dilatation of porcelain between 0° and 1040°, was found to be 0·0000108—that is to say, the same as between 0° and 860°.

In determining precisely the boiling-points of sulphur, cadmium and zinc by means of the air-thermometer, great difficulties arise from the fact that minute errors of weighing seriously affect the results, owing to the extremely small quantities by weight of air which remain in the apparatus at the temperatures employed. Deville and Troost have overcome this difficulty by employing iodine instead of air in the thermometer. The very considerable density of the vapour of iodine (8·7), and the fact that it has, fortunately without sensible error, the same coefficient of dilatation as air, render it invaluable for this purpose.

4. *Regnault's processes.*—The limits of this work will not permit the introduction of a complete account of the numerous processes devised by Regnault for determining the densities of the vapours of substances. The methods already described are capable of meeting every case likely to occur in chemical researches. It is true that instances sometimes present themselves where it is desirable to obtain information as to the physical characters of certain vapours, and their behaviour under various circumstances of temperature and pressure: in such cases it will be necessary to refer to the original memoirs; a list of some of the more important is therefore appended to this article. It would, however, be improper to omit a description of the following simple method, devised by Regnault (Ann. Ch. Phys. [3], lxiii. 53), for determining the densities of vapours at elevated temperatures. It is, however, only adapted for substances which are unacted on by air. The apparatus consists of two flasks, A A′, made of cast-iron, as nearly as possible of the same thickness. They are terminated by tubulures, which are closed by the bullets B B′, resting on the openings. The volumes of the two flasks are to be exactly determined by ascertaining the weight of water required to fill them. Some mercury is to be poured into the flask A; and in A′, the substance the vapour-density of which is to be ascertained. The apparatus is then to be placed on a muffle heated to a temperature somewhat more than sufficient to convert the substance into vapour. The mercury and substance soon enter into ebullition, expelling the air by the apertures, which are only imperfectly closed by the bullets. When the apparatus has been sufficiently heated, it may be removed and allowed to cool. The weights of the mercury remaining in A, and of substance in A′, are then to be determined by analysis.

Fig. 767.



Let P be the weight of the mercury,

P′ that of the substance,

δ the density of mercury compared with that of air under the circumstances of temperature and pressure which existed in the muffle at the moment of removing the apparatus.

The density of the vapour will be under the same conditions, and, assuming the volumes of the two flasks to be identical,

$$x = \delta \frac{P'}{P}.$$

But as, in practice, the capacities of the two flasks will never be exactly the same, we must substitute the following formula for that given by M. Regnault. Representing, therefore, the volume of *A* by *V*, and the volume of *A′* by *V′*, we have:—

$$x = \delta \frac{P'}{P} \cdot \frac{V}{V'}.$$

It is proper to remark that this method ceases to be accurate if there be any great difference between the volumes of *A* and *A′*.

The relations between the atomic weights of substances and their densities in the state of vapour or gas, have been so fully discussed in the article ATOMIC WEIGHTS (i. 466), that we only now have to consider the *method of calculating the theoretical* *vapour-density of a substance.* This may at once be obtained by multiplying the atomic weight of the substance by half the density of hydrogen, 0·034635. If the results of experiment differ from the number so obtained by a very large amount, it will probably arise from the vapour-density being anomalous. (See Atomic Weights.)

List of some Memoirs on Vapour-densities and Kindred Subjects.

Regnault: *Note on some Apparatus for determining the Densities of Gases and Vapours,* Ann. Ch. Phys. [3], lxiii. 45.—*Apparatus for the Determination of the Vapour-densities of Substances which boil at high Temperatures,* ibid. 53.—*Note on a Gas-Thermometer employed as a Pyrometer for measuring high Temperatures,* ibid. 39.

Hofmann: *Remarks on anomalous Vapour-densities,* Proc. Roy. Soc. x. 596.

Playfair and Wanklyn: *On a mode of taking the Density of Vapours of Volatile Liquids at Temperatures below Boiling-point,* Trans. Roy. Soc. Edin. xxii. Part iii. 441.

Natanson: Ann. Ch. Pharm. xcviii. 301.

Wurtz: *An Introduction to Chemical Philosophy according to the Modern Theories,* Chem. News, April 7, 1865.

Deville and Troost: *On Vapour-densities at very high Temperatures,* Ann. Ch. Phys. [3] lviii. 257.

Wurtz: *Determination of the Specific Gravities of Methylamine and Ethylamine at varying Temperatures and Pressures,* Mémoire sur les ammoniaques composées, tome xi. des Mémoires présentés par divers savants à l'Académie des Sciences, 1851.

Williams, C. G.: *Modes of determining Specific Gravities of Vapours, &c.*—Chemical Manipulation, p. 94.

Brown, Jas. T.: *Tables for the Calculation of Vapour-density Determinations,* Chem. Soc. J. [2], iv. 72.

Williams, C. G.: *Determination of Residual Air,* Phil. Trans. 1857, p. 460.

C. G. W.

SPECTRAL ANALYSIS. The examination of the properties of the light emitted by substances in the state of glowing gas has been termed Spectral Analysis. By this method we not only succeed in obtaining a much more accurate knowledge than we have hitherto possessed concerning the chemical composition of terrestrial matter, but we acquire information respecting the chemical nature of the sun, fixed stars, and distant nebulæ, opening out the new sciences of solar and stellar chemistry.

If, by means of a prism and suitable optical arrangements, we examine the light emitted by *incandescent solid* or *liquid* bodies, we find, first, that all such bodies become luminous at the same temperature; and, secondly, that when they first become luminous red rays alone are emitted, and that as the temperature rises, rays of every higher degree of refrangibility, up to a certain limit, are likewise given off, until, when the highest temperature is reached, all the luminous rays are emitted, and the body is said to be white-hot. Hence the spectrum of every incandescent solid or liquid is *continuous,* and cannot be used as a means of detecting the chemical nature of the substance. The light emitted by *incandescent gases* differs essentially from that radiated from solids or liquids, inasmuch as the spectrum of a glowing gas is *not continuous,* but consists of distinct bands or lines of light; in other words, is made up of different rays of definite degrees of refrangibility. Another difference to be noted is that, except in certain cases to be spoken of hereafter, the *quality* of the light of a glowing gas does not alter with increase of temperature: thus, as soon as sodium-vapour becomes luminous, it emits yellow light, nor can this colour be changed by increasing the temperature; sodium-vapour cannot be made white-hot.

Each elementary substance in the state of gas produces a spectrum consisting of bright lines or bands, which are unalterable in position, and are produced by that particular element alone; hence this property may be made use of for detecting the presence of the substance in question, and it matters not how far distant the source of light may be from the observer, provided the lines can be distinctly seen. Many chemical compounds are not decomposed below the temperature at which their vapours become luminous, and these compounds yield spectra differing from those of their constituent elements; in some cases a further elevation of temperature produces a sudden dissociation of the combined elements, and then the true elemental spectra become for the first time apparent—no further change in the position of the lines occurring with subsequent increase of temperature. In many instances, however, even in the case of the elemental lines, increase of temperature renders new lines visible, which could not be seen before, possibly owing to their not possessing sufficient intensity.

The methods of obtaining the spectra of the elements, or their compounds, differ according to their volatility. The instrument or spectroscope employed varies according to the degree of accuracy which the observations require: thus, for the detection of some of the more commonly-occurring substances, a rough apparatus with one prism will suffice, whereas for exact experiments, and for researches on solar chemistry, a much more powerful and optically perfect instrument is needed.

Examination of the Spectra of Bodies which tint the colourless Gas-flame.

It has long been known that certain substances, especially the salts of the alkalis and alkaline earths, tint the blowpipe-flame, and these tints have long been used as tests for the presence of the substances. Bunsen and Kirchhoff (1860, *Chemical Analysis by Spectrum Observations*: First Memoir, Pogg. Ann. cx. 161; and Phil. Mag. [4] xx. 89: Second Memoir, Pogg. Ann. cxiii. 337; and Phil. Mag. [4] xxii. 329 and 498) were the first successfully to apply the prism to the examination of these tints, whereby the accuracy and delicacy of their indications were infinitely increased, and thus to found the science of Spectral Analysis.

The improved spectroscope employed in these experiments is represented in *fig.* 768. On the upper end of the cast-iron foot, F, a brass plate is screwed, carrying the flint-glass prism P, having a refracting angle of 60°. The collimator-tube, A, is also fixed to the brass plate; in the end of this tube nearest the prism is placed a lens, whilst the other end is closed by a plate, in which a vertical slit has been made. Two arms are also fitted on to the cast-iron foot, so that they are moveable in a horizontal plane about the axis of the foot. One of these carries the telescope B, having a magnifying power of eight, whilst the other carries the tube C; a lens is placed in this tube at the end nearest the prism, and at the other end is a scale, which can be seen through the telescope by reflexion from the front surface of the prism. This scale is a photographic copy of a millimetre-scale, which has been produced in the camera of about $\frac{1}{15}$ the original dimensions. The structure of the slit is seen in *fig.* 769: the upper half only is left free; the lower half is covered by a small equilateral glass prism, which sends by total reflexion the light of the lamp D through the slit, whilst the rays of the lamp E pass freely through the upper and uncovered slit. By help of this arrangement, the observer sees the spectra of the two sources of light immediately one under the other, and can thus easily determine at a glance whether the lines are coincident or not. The instrument is used as follows:—In the first place, the telescope B is drawn out so far that a distant object is plainly seen; it is then screwed into the ring in which it is held, care being taken to loosen the screws α and β beforehand. The tube A is then brought into its place, and the axis of B brought into one straight line with that of A. The slit is then drawn out until it is distinctly seen

Fig. 768.

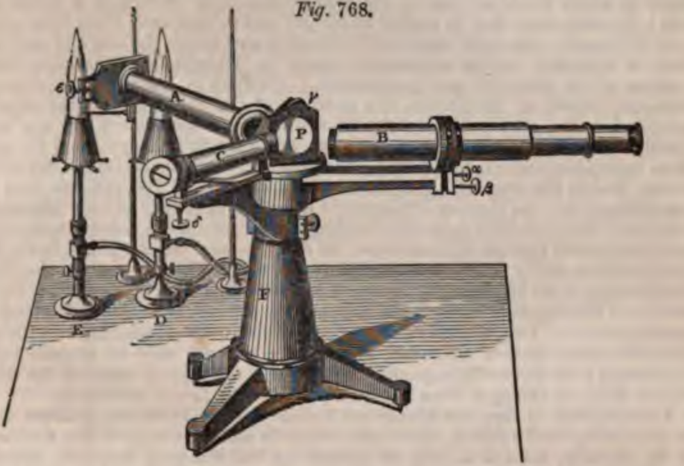
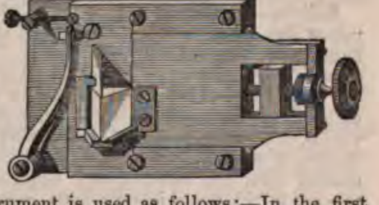


Fig. 769.



on looking through the telescope, and this latter is then fixed by moving the screws α and β until the middle of the slit is seen in the middle of the field of view. After removing the small spring γ, the prism is next placed on the brass plate, and fastened in the position which is marked for it, and secured by screwing down the spring-clamp γ.

If the axis of the tube A be now directed towards a bright surface, such as the flame of a candle, the spectrum of the flame is seen in the lower half of the field of the telescope, on moving the latter a certain angle round the axis of the foot F. When the telescope has been placed in position, the tube C is fastened on to the arm belonging to it; and this is turned through an angle such that, when light is allowed to fall on the divided scale, the image of the scale is seen through the telescope B, reflected from the nearer face of the prism. The divisions can easily be focussed, and the line on which the divisions lie brought parallel with the line dividing the two spectra by means of the screw (δ); a small gas-flame is then placed opposite the tube C to illuminate the scale. The breadth of the slit can be regulated, by means of the screw ϵ, according to the degree of illumination present, or the purity of the spectrum required. A black cloth, with holes for the tube C, is thrown over the whole apparatus to shade off stray light. In order to bring the two sources of light, D and E, into position, the following method may be employed :—If the lamp E be pushed past the slit, a point is easily found at which the blue lines of the hydrocarbon-flame (Swan, p. 358) are plainly seen; the lamp must then be pushed to the left still farther, until these lines nearly or quite disappear; the right mantle of the flame is now before the slit, and into this the bead of substance under examination must be brought. In the same way the position of the flame (D) may be ascertained (Bunsen). Owing to variations in the refracting power of the prisms, the positions of the lines of the same substances, measured by the photographic scale, on two different instruments will not coincide exactly. Bunsen has, however, given (Pogg. Ann. cxix. 6) an easy method for reducing these variations, rendering comparable the measurements thus made with different instruments. He has also proposed a graphical method (shown in *fig.* 770, opposite page 382) of mapping not only the position of the bright lines, but also their relative intensities and degrees of sharpness: this consists in shading in the lines under a millimetre-scale (representing that seen through the telescope), the starting-point being taken to be the D lines, the position of which is always represented at 50 mm. The height of the shading gives the intensity of the bright band, the extent of the shading gives the breadth of the line or band, and the degree of sharpness is indicated by the sudden or gradual growth of the shaded portions. This method cannot, of course, give to one unfamiliar with the spectra themselves, any idea of their real appearance; this can only be attained (and but imperfectly) by chromo-lithographic tables, which accompany some of the memoirs, and of which an enlarged series has been published by Lenoir of Vienna.

The discovery of four new elementary bodies (cæsium, rubidium, thallium, indium), by help of spectral analysis, since 1860, serves to show the value of this new method; of its delicacy, some idea may be formed by the following numbers, which give, in fractions of a milligramme, the weights of the smallest quantities of the metals in question which can thus be detected with certainty:—

	mgm.		mgm.
Sodium	0·0000003	Thallium	0·00002
Lithium	0·0000009	Rubidium	0·0002
Calcium	0·00001	Potassium	0·001
Cæsium	0·00005	Barium	0·001
Strontium	0·00006		

Spectrum Reactions of the Metals of the Alkalis and Alkaline Earths.

Sodium.—The spectrum-reaction of this metal is the most delicate of all. The yellow line, Na α, is the only one which appears in the sodium-spectrum as seen in the flame with the ordinary spectroscope. Examined at the high temperature of the electric spark with a more powerful set of prisms, this yellow line is seen to be double, and it is found to be exactly coincident with the dark double solar line known as D; under these circumstances, three other pairs of lines and a nebulous band become visible, in addition to the yellow D lines (Huggins, Phil. Trans. 1864, p. 139, on *The Spectra of some of the Chemical Elements*). The line Na α is remarkable for its exactly-defined form and extraordinary brightness. If the quantity of sodium-compound present in the flame is very large, some portion is precipitated in the solid form, and this gives rise to a faint continuous spectrum stretching at each side of the double yellow line; if a small piece of the metallic sodium be volatilised in the flame, the important phenomenon of the *reversal* of the sodium-spectrum is observed—that is, the *bright* sodium-lines on a *dark* background become changed to a *dark* one upon a background of a *bright* continuous spectrum. The explanation of this will be given hereafter. All the sodium-compounds yield the yellow line when heated in the flame; those (such as the oxides, chloride, iodide, bromide, sulphates, and carbonates) which are easily volatilised give the reaction most vividly, but the non-volatile phosphates, silicates, and borates also exhibit the line plainly. Swan in 1857, and indeed Melville in 1752, pointed out the delicacy of this reaction. The $\frac{1}{3000000}$ part of a milligramme of soda can be easily detected, and this reaction shows the constant presence of sodium-compounds floating about as motes in the sunbeam; all bodies, after exposure to the air for a few minutes, exhibit the soda-lines on ignition. This dust of sodium-compounds is derived from the evaporation of the minutely-divided particles of sea-spray, and from the transportation of the infinitely small solid particles by the winds.

Lithium.—The luminous vapour of lithium, obtained by the ignition of the salts of this metal in the flame, yields a spectrum consisting of two bright lines: the one a bright red line, Li α (31 mm. on Bunsen's scale), and the other a very much less distinct orange line, Li β (45 mm. on Bunsen's scale). When lithium-vapour is more strongly heated, as in an oxyhydrogen-flame or in the electric discharge, a blue line or band becomes visible, in addition to the other two lines which do not change their position (Tyndall and Frankland, Phil. Mag. [4], xxii. 472). This new blue lithium-line, when viewed with one prism, appears coincident with the blue strontium-line, Sr δ (see p. 380). On examination with three prisms and a high magnifying power, the blue lithium-line is seen to be somewhat more refrangible than the strontium, δ, the lines being separated by a space about equal to that separating the two sodium-lines. (Roscoe and Clifton, Proc. Manch. Phil. Soc. 1861–62, p. 227.)

All the lithium-compounds give the reaction; indeed, minerals containing lithium (such as triphylline, triphane, and petalite) only require to be held in the flame to exhibit the red line, Li α, most distinctly. Lithium-compounds were formerly supposed to occur most sparingly on the earth's crust, but spectral analysis has shown that this metal is most widely diffused. It has been found in the waters of the Atlantic, in the ashes of marine plants, in all the quartz and orthoclase of the Odenwald, as well as in very many other minerals from different localities; in almost every mineral-water, as well as in almost all well- and river-waters; in the ashes of tobacco, of wood of the vine; in milk, coffee, tea; in human blood, and in muscular tissue. Lithium-salts have been found to occur in large quantities in a spring in Cornwall (W. A. Miller, Brit. Assoc. Report, 1864). Lithium has also been found in meteoric stones. (Bunsen, Ann. Ch. Pharm. cxx. 253.—Engelbach, Pogg. Ann. cxvi. 512.)

Potassium.—Volatile potassium-compounds, when placed in the flame, give a widely-extended continuous spectrum, which consists of two chief lines: one line, K α, situated in the outermost red (from 16·5 to 18·5 on Bunsen's scale), and a second line, K β, situated far in the violet rays towards the other end of the spectrum (152·5 to 153·5 on Bunsen's scale). When the vapour of potassium is heated in the electric spark, several other lines make their appearance (Huggins). All potassium-salts containing volatile acids exhibit the two lines when placed in the flame, but the potash-silicates and some other non-volatile compounds do not show it, and must therefore be ignited with sodium-carbonate. The presence of the sodium-salt does not interfere with the reaction, and scarcely diminishes its delicacy. Orthoclase, sanidine, and adularia may in this way be easily distinguished from albite, oligoclase, labradorite, and anorthite. If only a trace of potash is present, the silicate must be heated with ammonium-fluoride in a platinum-basin, and the residue brought into the flame on a platinum-wire.

The potassium-red line, K α, was at one time supposed to be coincident with Fraunhofer's line A (Kirchhoff, *Researches*, part i.); it has since been shown that the red line is a double one (Roscoe), and that it is not coincident with Fraunhofer's A. (Kirchhoff, *Researches*, &c., part ii.)

Rubidium and Cæsium.—These two new alkali-metals were discovered by Bunsen in the mineral-water of Dürkheim, and in Saxon lepidolite (Berlin. Acad. Ber. 10 Mai 1860, p. 221; Chem. News, iii. 132). Since their discovery they have been found to be widely diffused; indeed, rubidium may be said to be a commonly-occurring substance; for although it exists only in small quantities, it is met with in a large number of mineral waters, and in the ashes of many vegetables, such as tobacco, coffee, and beetroot (Grandeau, Compt. rend. liv. 450, 1057). The chemical properties of the cæsium-compounds, together with the methods employed for the separation of this metal from rubidium, are described in vol. i. p. 1112 of this Dictionary; the rubidium-compounds are noticed in vol. v. pp. 127–131; hence it will here only be necessary to describe their spectra.

The spectra of the new metals exhibit, in the first place (in accordance with their correspondence in other chemical properties), a striking analogy with the potassium-spectrum; all three metals possess spectra which are continuous in the centre, decreasing in intensity towards each end. In the case of potassium, the continuous portion (indicated in the mass by a dark band *above* the division) is most intense, in that of rubidium less intense, and in the cæsium-spectrum this luminosity is least. In all three we observe the most intense and characteristic lines towards both the red and blue ends of the spectrum. Of the *rubidium-lines*, those marked Rb α and Rb β (137 and 135—136 mm.) are the most brilliant, and best suited for the recognition of the metal. Less brilliant, though still characteristic, are the red lines Rb γ and Rb δ (15—16 and 13—14 mm.), from which the metal derives its name; they are remarkable as both being less refrangible than the potassium red lines K α, and the outer one of them lies so far in the dark red as to be only rendered visible by a special arrangement. The other lines, which are found on the continuous portion of the spectrum, cannot so well be used as a means of detection, because they only appear when the substance is very pure, and when the degree of illumination is very great. The nitrate, chloride, chlorate, and perchlorate, on account of their easy volatility, show these lines most distinctly; but even the least volatile rubidium-compounds, such as the silicates, yield spectra in which all these details are plainly seen.

The *spectrum of cæsium* is chiefly characterised by the two lines Cs α and Cs β (109 and 106 mm.), remarkable for their brilliancy and sharpness of definition, as well as by the absence of any line in the red as in the two other spectra. The line Cs γ in the orange (42 mm.) is the next most distinct. The other yellow and green lines marked on the map first appear when the luminosity is great; and though they cannot be used for detecting the presence of small quantities of the cæsium-compounds, they may serve with advantage as tests of the purity of the cæsium-salt under examination, as they are seen only when all foreign matter is got rid of.

The delicacy of the spectrum-test for the pure compounds is, for rubidium 0·0002 mgm., and for cæsium 0·00005 mgm.; if other members of the alkaline group of metals be present, the delicacy of the reaction is of course impaired; but even when mixed with from 300 to 400 times its weight of the chlorides of potassium and sodium, the cæsium-chlorides would be easily detected; whilst the rubidium-salt will bear dilution with from 100 to 150 times its weight of the common alkalis before its spectrum is rendered indistinct. (Bunsen.)

The following is a list of the chief sources in which the new alkaline metals have as yet been found:—

In mineral waters:—Durkheim, Kissingen, Nauheim, Kreuznach, Baden-Baden, Wiesbaden, Soden near Frankfort, all contain both metals: see the Second Memoir by Bunsen and Kirchhoff.

Vichy, Bourbonne. (Grandeau, Compt. rend. liii. 1100.)

Ebensee, Haller, Gastein. (Redtenbacher, J. pr. Chem. lxxxv. 458.)

Aussee. (Schrötter, *ibid.* p. 458.)

Topusco, Lassinga, Karlsbrunn. (Schneider, *ibid.* p. 458.)

Salins (Jura), Contrexéville (Vosges).

Dead Sea water. (Grandeau, Ann. Ch. Phys. [3], lxvii. 175.)

In minerals:—Lepidolite from Roxena, Cs and Rb. (Bunsen and Kirchhoff.)

Lepidolite from Hebron in Maine, Rb and Cs. (O. D. Allen, Phil. Mag. [4], xxv. 189).

Lepidolite from Prague, Petalite from Uto, Rb and Cs. (Grandeau, Ann. Ch. Phys. [3], lxvi. 172, 173.)

Triphylline, Rb and Cs. (Bunsen, Chem. News, iv. 163.)

Lithia-mica from Zinnwald in Bohemia, Rb and Cs. (Bunsen, Chem. News. iv. 286.—Schrötter, J. pr. Chem. lxxxv. 458.)

Gneiss from Freiberg, Rb. (Rube, Berg- und Huttemänn. Zeitung, 1862, No. 8, p. 75.)

Carnallite, Rb and Cs. (Erdman, J. pr. Chem. lxxxvi. 377.)

Orthoclase from Carlsbad, Rb. (Erdman, *ibid.* p. 448.)

Chile saltpetre. (Bunsen, Pogg. Ann. cxiii. 361.—Grandeau, Ann. Ch. Phys. [3], lxvii. 207.)

Pollux from Elba (Pisani, Compt. rend. lviii. 714) contains 34 per cent. of cæsium; in all former analyses of the mineral this had been taken for potassium.

In vegetables and vegetable products, rubidium alone is found.

In beetroot and the saltpetre derived from it:—Grandeau (Compt. rend. liv. 450; Ann. Ch. Phys. [3], lxvii. 201).—Lefebre (Compt. rend. lv. 430).

In tobacco (Havana and Kentucky), in coffee, tea, cream of tartar.

In the ash of the oak-tree, *Quercus pubescens*. (Von Thann, J. pr. Chem. lxxxvi. 254.)

Strontium.—The spectra of the alkaline earths are by no means so simple as those produced by the alkalis; that of strontium is characterised by the absence of green bands. Eight lines in the strontium-spectrum are remarkable—six red, one orange, and one blue line: of these the orange, Sr α (45—47 mm.), two red, Sr β and Sr γ (31·5—33 and 33·5—34·5 mm.), and the blue line, Sr δ (104·5—105·5 mm.).

The chloride and other haloid salts of strontium give the best reaction, whilst it is seen less distinctly with the sulphate and carbonate, and cannot be obtained at all with the non-volatile compounds. On moistening the bead with hydrochloric acid, the lines are seen more vividly; the sulphate must previously be reduced to sulphide by holding the bead in the reducing flame, and the silicates must be fused on a platinum-loop, with carbonate of sodium, and the fused mass powdered, and washed on a plate by decantation. The insoluble carbonate of strontium is thus obtained, of which one or two-tenths of a milligramme, brought on to a platinum-wire and moistened with hydrochloric acid, suffices to give the most distinct reaction. The strontium-lines do not interfere with the indications of potassium and sodium; and lithium can also be detected in presence of strontium when the proportion of the former metal is not very small. The lithium-line appears as an intensely red and sharply-defined line upon a less distinct red ground of the broad strontium-band, Sr β. (Bunsen and Kirchhoff.)

If the temperature of the incandescent strontium-compounds be greatly increased, as when they are volatilised in the intense induction-spark, a sudden change in the spectrum is noticed, especially if a more powerful spectroscope is employed. Not only do new lines thus become visible which were not seen in the flame-spectrum, but the broad *bands*, characteristic of the spectrum at the lower temperature, totally disappear, and a mass of fine bright *lines* supply their place. These are, however, not coincident with any part of the band, being sometimes more and sometimes less refrangible. The lines, Sr α, β, γ disappear in the intense spark, whilst the blue line, Sr δ, does not alter either in intensity or in position with the alteration of temperature, but four new violet lines make their appearance. An explanation of this phenomenon of the disappearance of the broad bands and the production of the bright lines may be given by the supposition that the glowing vapour at the low temperature consists of the oxide or other compound of the difficultly reducible metal, whereas, at the enormously high temperature of the intense spark, these compounds are decomposed, and the true bright lines of the metal-spectrum are obtained (Roscoe and Clifton, Proc. Manch. Society, 1861–62, p. 227). The bright lines of metallic strontium have been carefully mapped by Huggins (*loc. cit.*).

Kirchhoff states in his memoir (Part i. p. 11) his opinion that the position of the bright bands, or maxima of light, is not dependent upon the temperature, upon the presence of other vapours, or upon any other condition except the chemical constitution of the vapour. The appearance of the spectrum may, however, Kirchhoff states, be very different under different circumstances. "Even the alteration of the mass of the incandescent gas is sufficient to effect a change in the character of the spectrum. If the thickness of the film of vapour whose lines are being examined be increased, the luminous intensities of all the lines increase, but in different ratios. The intensity of the bright lines increases more slowly than that of the less visible rays. The impression which a line produces on the eye depends on its breadth as well as its brightness. Hence it may happen that one line being less bright, although broader than a second, is less visible when the mass of incandescent gas is small, but becomes more distinctly seen than the second line when the thickness of the vapour is increased. Indeed, if the luminosity of the whole spectrum be so lowered that only the most striking of the lines are seen, it may happen that the spectrum appears to be totally changed when the mass of the gas is altered. Change of temperature appears to produce an effect similar to this alteration in the mass of the glowing vapour, no deviation in the maxima of light being observed, but the intensities of the lines increasing so differently, that those most visible at a high temperature are not those most readily seen at a low temperature" (Kirchhoff). Although this explanation of the changes observed may certainly apply to many cases, yet there can be no doubt that experiments made since the foregoing opinion was expressed, prove that in most instances the changes which occur are sudden, and are due to an alteration in the chemical constitution of the incandescent vapour.

Calcium.—The spectrum of this metal is immediately distinguished from all the preceding by the characteristic green band, Ca β (57 to 62·5 mm.), and by the orange band, Ca α (39·5 to 44 mm.). The chloride, iodide, and bromide give the reaction best; the non-volatile calcium-compounds must be decomposed either by hydrochloric acid, or by ammonium-fluoride, before the spectrum can be plainly obtained; and then, if the quantity of metal present be very small, the characteristic lines are seen to flash out only for a moment as the salt rapidly becomes basic and non-volatile. In this way, either by heating the substance alone, or after treatment with hydrochloric acid or ammonium-fluoride, the mineralogist and geologist is provided with a simple method of recognising the components of a minute fragment of substances with an ease and certainty attained in the ordinary method only by a large expenditure of time and material. Examples of the application of these tests are given in Bunsen and Kirchhoff's second memoir: these prove that some limestones contain lithium and strontium, as well as sodium and potassium; and it is probable that an exact series of experiments on the amount of these ingredients contained in these various limestones may prove of the highest geological interest, both as regards the order of their deposition and their local distribution. The calcium-spectrum shows the same kind of remarkable change on increase of temperature as the strontium-spectrum (Kirchhoff, *Researches*, i. 12); thus the broad band, Ca β, is replaced in the intense spark-spectrum by five fine green lines, all of which are less refrangible than any part of the band Ca β, whilst in place of the orange band, Ca α, three more refrangible orange lines are seen. The total disappearance in the spark-spectrum of a well-defined yellow band seen in the flame-spectrum at the lower temperature was strikingly evident (Roscoe and Clifton). The spark-spectrum of calcium contains also two bright lines in the violet, which may coincide with the two solar lines known as Fraunhofer's H. (Huggins.)

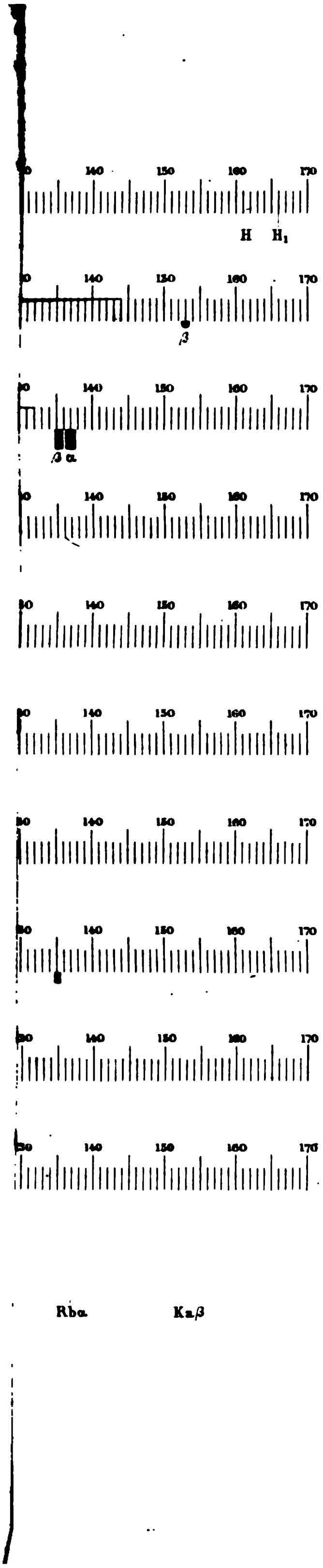
Barium.—This is the most complicated of all the flame-spectra of the alkalis and alkaline earths. It is at once distinguished from all the others by the green bands, Ba α (69·5 to 73 mm.) and Ba β (75 to 79 mm.); these are by far the most distinct, appearing at the first, and continuing during the whole of the reaction. Ba γ (59 to 63 mm.) is not quite so distinct, but is still a well-marked and peculiar line. The chloride, bromide, iodide, and fluoride, as well as the hydrate, carbonate, and sulphate, yield the reaction; the silicates must be treated previously with hydrochloric acid, or fused with sodium-carbonate, and the resulting barium-carbonate dissolved in acid. If barium and strontium occur in small quantities together with large amounts of calcium, the carbonates obtained by fusion are dissolved in nitric acid, and the dried salt exhausted with alcohol. The residue contains only barium and strontium, both of which can be almost always detected.

Unless one or more of the bodies to be detected is present in very small quantities, the methods of separation just mentioned are quite unnecessary, as a simple inspection of the flame-spectrum generally exhibits the bright lines of the various substances, appearing one after the other in the order of their volatility, and dying gradually out again as the pictures in a dissolving-view. The absence of any one or of several of these bodies is at once indicated by the non-appearance of the corresponding bright lines (Bunsen and Kirchhoff). The same phenomenon of change from broad bands to fine lines on increase of temperature has been observed in the barium as in the two foregoing spectra.

The spectrum of magnesium, as well as the spectra of almost all the other metals, cannot be obtained by means of the flame, owing to their compounds being non-volatile at the temperature of burning coal-gas. In order to obtain the spectra of these substances, recourse must be had to the method with the electric spark, explained hereafter.

Thallium.—The compounds of this new metal, discovered by Mr. Crookes (Chem. News, March 30, 1861) in certain specimens of iron-pyrites, give when brought into the flame, a splendid green coloration, and this yields a spectrum consisting of one green line, Tl α (77·5 to 78 mm.), which coincides with a part of the green barium-band, β. When examined with one prism, the extreme brilliancy of this line renders the detection of traces of thallium in pyrites easy (see the article THALLIUM in this volume; also Crookes, Phil. Trans. 1863, p. 173). When the spark-spectrum of thallium is examined, five lines are observed, in addition to the intense one in the green; first a very faint one in the orange; next two of nearly equal intensity in the green, more refrangible than Tl α, with a third much fainter, these lines being nearly equidistant; whilst fifth in the blue is a bright well-defined line (W. A. Miller, Proc. Roy. Soc., 1863, p. 407). Gassiot (Proc. Roy. Soc. xii. 536) found that the two green thallium- and barium-lines do not coincide when examined with a magnifying power of 80.

Indium.—This metal was discovered by Drs. Reich and Richter in the Freiberg zincblende (Phil. Mag. [4], March 1864, xxvii. 199). Its compounds are recognised by the deep indigo-coloured tint which they impart to flame. The indium-spectrum is characterised by two blue lines, which are best seen when a bead of an indium-compound is held between two electrodes from which a spark passes. The lines In α and In β fall respectively upon divisions 107·5 and 140 mm. of the photographic scale of the spectroscope when Na $\alpha = 50$ and Sr $\delta = 100·5$. The specific gravity of the metal is 7·277, and its atomic weight about 37 = In (monatomic). (Reich and Richter, J. pr. Chem. xcii. 480; see p. 268, vol. iii. of this Dictionary; also Strong, Berg- und Hüttenm. Zeit. 1865, p. 191; A. Winkler, J. pr. Chem. xciv. 1; Weselsky, Wien. Acad. Berichte, li. 286, May 1865.)


130
140
150
160
170
H
H₁
β
β α
Rbα
Kaβ

Although Bunsen and Kirchhoff have the merit of founding the method of spectral analysis, inasmuch as they placed it on a complete scientific basis, yet previous observations on this subject had not been wanting. Thus, so long ago as 1752, Thomas Melville pointed out the peculiar nature of certain coloured flames, and observed the yellow soda-flame, although unacquainted with its cause. In 1822 Brewster proposed his monochromatic lamp, but the first idea of this is due to Melville. In 1822 Sir John Herschel (Phil. Trans. p. 455) investigated the spectra of many coloured flames (muriates of strontia and lime, nitrate of copper, and boracic acid), and he writes in 1827 about them as follows, in the *Encyclopædia Metropolitana*: "The colours thus communicated by different bases to flame afford in many cases a ready and neat way of detecting extremely minute quantities of them." Fox Talbot, writing in 1826, makes the following valuable suggestions respecting these spectra: "The red fire of the theatres, examined in the same way, gave a most beautiful spectrum, with many light lines or maxima of light; in the red these rays were more numerous, and crowded with dark spaces between, besides an exterior ray greatly separated from the rest, and probably the effect of the nitre in the composition" (really K α). "In the orange was one bright line, one in the yellow, three in the green, a very bright one in the blue, and several that were fainter. . . . If this opinion (about the formation of these lines) should prove correct, and applicable to the other definite rays, a glance at the prismatic spectrum of a flame might show it to contain substances which it would otherwise require a laborious chemical analysis to detect."

These early observers, however, got altogether wrong with respect to the soda-reaction, and hence they cannot be considered in any way to have founded the science of spectrum-analysis. Thus Herschel says that he found "that when sulphur is thrown into a white-hot crucible, a very large quantity of a definite and purely homogeneous yellow light is produced," and that "Dr. Brewster obtained the same yellow light by setting fire to spirits of wine diluted with water and heated." Talbot states: "Hence the yellow rays may indicate the presence of soda, but they nevertheless frequently appear where no soda can be supposed to be present." He then mentions that the yellow light of burning sulphur is identical with the light of a spirit-lamp with a salted wick, and states that he is inclined to believe that the yellow light which occurred when salt was strewed upon a platinum-foil and placed in a flame, "was owing to the water of crystallisation rather than the soda." He is puzzled to know why, if this be the case, the same result is not obtained with salts of potash; he then finds that wood, ivory, paper, &c. give more or less of this yellow light, always the same in its characters. The only principle which these have in common is *water*, and yet he doubts whether water can cause this yellow light, as ignited sulphur produces the same. At one part of his paper he attributes this yellow colour to soda-salts, and in another part he says: "The bright line in the yellow is caused without doubt by the combustion of the sulphur." Talbot further on states that the "mere presence" of the substance, "which suffers no diminution in consequence," as in the case of chloride of calcium, causes a red-and-green line to appear in the spectrum. (See Kirchhoff, on *History of Spectrum Analysis*, Phil. Mag. [4], xxv. 250.)

In February 1834, Talbot writes (Phil. Mag. iv. 114): "Lithia and strontia are two bodies characterised by the fine red tint which they communicate to the flame. Now, it is difficult to distinguish lithia-red from strontia-red by the unassisted eye, but the prism displays between them the most marked distinction that can be imagined. The strontia-flame exhibits a large number of red rays, well separated from each other by dark intervals, not to mention an orange and a bright-blue ray. The lithia exhibits only one single red ray. Hence I hesitate not to say (referring to some experiments of Herschel), that optical analysis can distinguish the minutest portion of these substances from any other with as much certainty if not more than any other method." In 1845, W. Allen Miller (Phil. Mag. [3], xxvii. 81) published an investigation on the spectra of coloured flames, as well as the dark absorption-bands produced when white light passes through certain gases. Coloured diagrams of the spectra accompany the memoir, but, owing to the fact that the flame employed was a luminous one, these spectra are not distinctive enough of the particular substance to enable them to be used as characteristic tests for the metals in question. Amongst the spectra described and drawn are chloride of copper, boracic acid, nitrate of strontia, chloride of calcium, and chloride of barium; also the chlorides of sodium, manganese, and mercury, and of a large number of other metals.

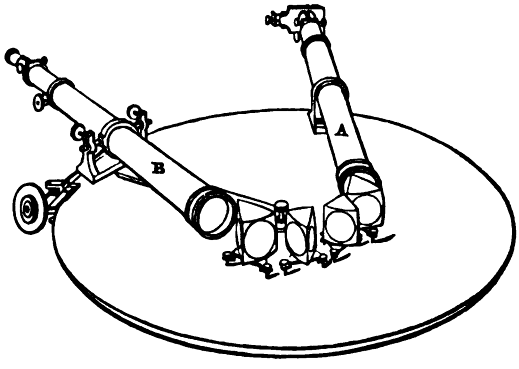
The first to point out the extreme delicacy of the spectrum-test for soda was Swan (Edin. Phil. Trans. xxi. 411), who showed that the reaction could be produced by $\frac{1}{2500000}$ part of a grain of common salt. And he concludes as follows: "When, indeed, we consider the almost universal diffusion of the salts of sodium, and the remarkable energy with which they produce yellow light, it seems highly probable that the yellow line R, which appears in the spectra of almost all flames, is in every case due to the presence of minute quantities of sodium." The following literature, in addition to the memoirs already cited on this part of the subject, may be consulted:—(1) *Lectures on Spectrum Analysis*, by W. A. Miller, Pharm. Journ. Feb. 1862; (2) Ditto by H. E. Roscoe, Chem. News, iii. 153, 170; *ibid.* v. 218, 261, 287.—Grandeau, *Instruction pratique sur l'Analyse Spectrale*, Paris, 1863.—Dibbits, H. C., *De Spectraal Analyse*, Rotterdam, 1863 (containing an able historical summary of the discoveries in the subject).—Mousson, *Résumé de nos Connaissances sur le Spectre*, Arch. Sc. Natur. de Genève. Mars. 1861.

Examination of the Spectra of Bodies volatilised in the Electric Spark.

This method is applicable not only to all those bodies which are non-volatile at the temperature of the colourless gas-flame, but also to those which are gaseous at the ordinary temperature (such as hydrogen), and require to be heated by the electric spark in order to be made incandescent.

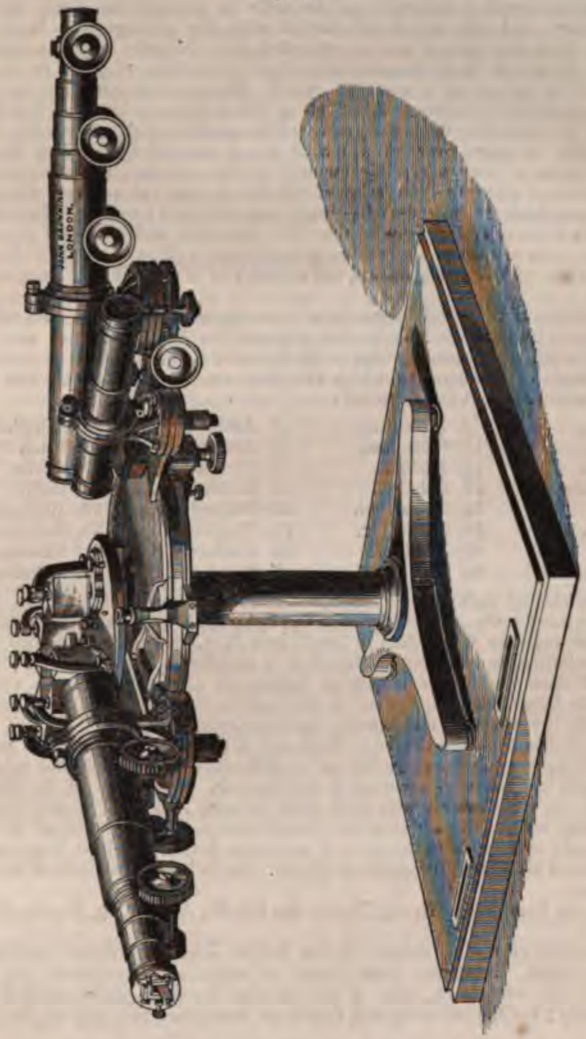
As the number of lines which become visible in the spectrum of the spark is very much larger than is seen in the flame-spectrum, a much more perfect and powerful spectroscope is needed for these observations. *Fig.* 771 represents the arrangement employed by Kirchhoff in his *Researches on the Solar Spectrum and Spectra of the Chemical Elements* (Macmillan, London, 1862 and 1863), and made by Steinheil of Munich. It consists of a collimator, A, screwed on to a planed circular iron table, and carrying the slit, formed of two knife-edges, the breadth of which can be regulated by a micrometer-screw. The slit itself can be brought into the focus of the achromatic object-glass by a rack-and-pinion motion. The telescope B, containing a similar objective, is fastened to a brass arm movable about the centre of the plate, either by the hand or with a micrometer-screw. Between the two objectives four flint-glass prisms are placed; the circular refracting surface on each is 18 Paris lines in diameter; three of them have a refracting angle of 45°, and the fourth of 60°. Each of the prisms is cemented on to a small brass stand with three set-screws. The telescope B, having a magnifying power of 40, has a horizontal motion with respect to the brass arm; it can be moved about a horizontal axis, and can be drawn in and out in the direction of this axis, as seen in the figure. In setting up this train of prisms, the greatest care must be taken, in the first place, that the axis of the two tubes are in the same horizontal plane, and parallel to that of the iron table; secondly, that the refracting surfaces of the prisms are all perpendicular to this plane; and thirdly, that the prisms are all placed at the angle of minimum deviation for the rays about to be observed (Kirchhoff). A large spectroscope, containing a powerful train of prisms, has been described by Gassiot (Proc. Roy. Soc. 1863, xii. 536), and known as the Kew spectroscope; and a second, containing eleven hollow prisms, filled with carbonic disulphide, is also described by Gassiot (Phil. Mag. [4] xxviii. 69). Wolcott Gibbs (Sill. Am. Journ. [2] xxxv. 110) has also described a large spectroscope. *Fig.* 772 exhibits the "Gassiot" spectroscope with four flint-glass prisms, as manufactured by Mr. Browning of the Minories. The arrangement employed by Huggins (Phil. Trans. 1864, p. 139), in his researches on the spectra of some of the chemical elements, was similar to that used by Kirchhoff; he employed six dispersing and one reflecting prism; the total deviation of the light in passing through the train of prisms was for the D ray 198°, and the distance traversed by the vernier of the telescope in passing from one of the D lines to the other was 75″.

Fig. 771.



Wollaston, who discovered the dark lines in the solar spectrum, was the first to observe the bright lines in the spectrum of the electric spark; but Faraday first asserted that the electric spark consisted solely of the material particles of the poles and of the medium through which it passes. **Wheatstone**, in 1835, showed that the spectra produced by the sparks from different metals were dissimilar, and he concluded that the electric spark results from the volatilisation and ignition, and not the combustion, of the ponderable matter of the poles itself, as the same phenomena were observed in hydrogen. **Wheatstone** (Abstract Brit. Assoc. Report, 1835) writes as follows, concerning the differences observable in the spectra produced by the poles of different metals: "These differences are so obvious, that one metal may instantly be distinguished from another by the appearance of its spark; and we have here a mode of discriminating metallic bodies, more readily applicable even than a chemical examination, which may hereafter be employed for useful purposes." **Angström**, in 1855 (Phil. Mag. [4] ix. 327), pointed out that a

Fig. 772.



twofold spectrum is always seen when we examine the electric spark, one set of lines being derived from the ignition of the particles of air or gas through which the sparks pass, whilst the second set is caused by the incandescence of the metallic particles themselves.

In order to obtain the spark easily and of the requisite degree of intensity, a powerful Ruhmkorff's induction-coil is used (Van der Willigen, Pogg. Ann. cvi. 615; see also p. 458 vol. ii. of this Dictionary); the one employed by Kirchhoff gave, by means of a moderately powerful battery, a spark 0·3 metre in length, whilst the coil used by Huggins gave a spark 3 inches long. In order to intensify the spark, the ends of the secondary coil are placed in contact with the coatings of a large Leyden-jar. The electrodes, also of course connected with the poles of the secondary coil, consist of the metals under examination, either in the form of wire, or of irregular pieces held by forceps on a moveable stand. Many precautions must be taken in working, especially with two different sets of electrodes, as it has been found that the currents of air, caused by the rapid passage of the electric spark between the electrodes, are sufficient to carry over to a second set of electrodes, placed at the distance of a few inches, a very perceptible quantity of the materials undergoing volatilisation. Hence no separate observation of the two spectra (at any rate where volatile metallic compounds are introduced as beads into the spark) can be relied on, unless one is made a considerable space of time after the other, and unless all the electrodes which have been once used are exchanged for new ones (Roscoe and Clifton). For further details of the arrangements, the memoirs of Kirchhoff and Huggins must be consulted.

The positions of the metallic lines have been mapped by Kirchhoff with reference to the dark solar lines, whilst Huggins has employed the bright air-lines as a constant scale upon which to note the position of the metal lines; but both experimenters use an arbitrary scale of divisions, by which the lines can be designated. The following elements were examined by Kirchhoff:

1. Sodium.
2. Calcium.
3. Barium.
4. Magnesium.
5. Iron.
6. Copper.
7. Zinc.
8. Chromium.
9. Strontium.
10. Cadmium.
11. Nickel.
12. Cobalt.
13. Potassium.
14. Rubidium.
15. Lithium.
16. Tin.
17. Antimony.
18. Arsenic.
19. Cerium.
20. Lanthanum.
21. Didymium.
22. Mercury.
23. Silicium.
24. Glucinum.
25. Aluminium.
26. Lead.
27. Silver.
28. Gold.
29. Ruthenium.
30. Iridium.
31. Platinum.
32. Palladium.

The spectrum of each of these metals contains a large number of lines, and these spectra are much more complicated than the flame-spectra: thus, in the green portion alone, there exist no fewer than 70 bright iron lines. Great care is needed, therefore, in the discrimination of metals, although it is easy for a trained eye to distinguish even such closely analogous metals as lanthanum and didymium, or erbium and cerium. In Kirchhoff's maps many of the metallic lines figure as broad bands; this is especially the case with the mercury- and zinc-spectra.

In Kirchhoff's maps the degree of blackness of the solar lines, and the relative intensities of the metallic lines, are denoted by different shades of the same colour, whilst their breadth is likewise represented in the drawing. The maps of the two experimenters do not agree exactly with each other, because Kirchhoff altered the position of his prisms several times during the measurements, in order to bring the different rays as nearly as possible to the point of minimum deviation, whilst Huggins allowed the position of his prisms to remain unaltered. The following metals have been mapped by Huggins:

Na, K, Ca, Ba, Sr, Mn, Tl, Ag, Te, Sn, Fe, Cd, Sb, Au, Bi, Hg, Co, As, Pb, Zn, Cr, Os, Pd, Pt.

In both sets of tables, several of the bright lines of different metals seem to coincide: when, however, these cases of apparent coincidence are narrowly observed in the instrument, most of the lines are found to show real differences of refrangibility; but the following still remain as unresolved coincidences (on Huggins's maps):

Zn, As 909 Na, Ba 1005 Os, As 1737.
Na, Pb 1000 Te, N 1366 Cr, N 2336.

Future research must prove whether these apparent coincidences are resolved on application of a still higher power.

For a description of the individual spectra of these metals, the above-mentioned memoirs and maps must be referred to, as it is impossible, by a brief description, to give any idea of the characteristic features of the masses of bright lines constituting these spectra.

The long Spectrum of the Electric Light.—Stokes (Phil. Trans. 1862, p. 599) has examined the spectrum of the electric spark when the lens and prisms are made of quartz; this substance allows rays of high refrangibility to pass, whereas glass cuts them all off. These rays are invisible to the eye, but can be rendered visible when allowed to fall on a fluorescent body, such as paper moistened with quinine-solution (iii. 633). On forming a pure spectrum of the electric spark from a Leyden jar, and receiving it on a highly fluorescent substance, the existence of rays of light was revealed, at a distance from the last visible violet rays, equal to six times the length of the whole visible spectrum. Each metal exhibits a peculiar series of these bands, and of all the metals, aluminium is found to be the richest in these rays of extreme refrangibility. These rays act chemically, and photographs of the invisible metal lines have been made by Miller (Phil. Trans. 1863, p. 1), whilst the same observer has determined the photographic transparency of different media (iii. 690).

Absorption Spectra.—This subject has already been sufficiently discussed (iii. 636). It only remains to notice a remarkable phenomenon lately observed by Bunsen (Pogg. Ann. cxxxvii. 100) in the absorption-spectrum of didymium. He finds that this spectrum undergoes an alteration if it be viewed by polarised light, according as the ordinary or the extraordinary ray is allowed to pass through the crystal. Bunsen also observed differences in the absorption-spectra of the various didymium-salts.

Projection of the Metal Spectra on a Screen.

The spectra of the metals can be thrown on a screen by help of a Duboscq's electric lamp (ii. 472). The metal or metallic compound of which it is desired to obtain the incandescent vapour, is placed in a small cup hollowed out in the lower carbon; on making contact with a battery of 50 to 60 Grove's cells, the metal is gradually vaporised, and the light passing through the slit and a lens is dispersed by two large prisms filled with carbonic disulphide. A continuously bright spectrum can thus be obtained from the incandescent carbon-points alone, and the presence of the several metals is indicated by the appearance of characteristic bright bands. In this way the bright bands of zinc and copper may be beautifully shown by volatilising brass, whilst silver, tin, and other metals yield their peculiar bands; the salts of the alkalis and alkaline earths, either separately or when mixed together, can also be made to exhibit their bright bands. The spectra thus obtained cannot, however, be compared for purity, fineness of detail, or exactness, with those received on the retina directly from the electric spark, and are therefore unsuited to the purposes of research, partly because the optical arrangement is necessarily imperfect, and also because the impurities (consisting of sodium, lime, &c.) always present in the gas carbon-points, render the spectrum impure. Debray has proposed (Ann. Ch. Phys. [3], lxv. 331) to employ the oxy-hydrogen-flame as the source of heat for the volatilisation of the metals; the projected spectra thus obtained are, however, necessarily much inferior to the electric spectra in brilliancy and distinctness.

The spectra of certain solid elements—such as silicon, sulphur, carbon, phosphorus, &c.—cannot be satisfactorily obtained by means of the ordinary electric spark—either (in the case of silicon, see Kirchhoff) because they cannot be volatilised, or because they yield solid oxidation-products, such as phosphoric pentoxide, giving a continuous spectrum. These latter elements must be vaporised, and their rarefied vapours ignited by the passage of the induction-spark through vacuum-tubes.

Examination of the Spectra of Bodies which are Gaseous at the ordinary Temperatures, or which require to be heated in Vacuum Tubes.

The spectra of the gases can be obtained either—(1) by passing the electric spark, from poles of some metal whose lines are known, through the gas in question, under the common atmospheric pressure; or (2) by observing the spectrum of the induction-spark, passing through a capillary tube (by Geissler's tubes, ii. 390, 472, &c.) containing the gas in an extremely rarefied state. The first of these methods has been followed by Kirchhoff and Huggins (*loc. cit.*), and the second by Plücker. (Pogg. Ann. März 1858, vol. civ.; *ibid.*, Aug. 1858, vol. cv.; *ibid.*, May 1859, vol. cvii. pp. 497, 638; also Plücker and Hittorf, Phil. Trans. 1865, p. 1.)

Spectrum of Atmospheric Air.—The air-lines are present with all electrodes, when the spark is taken in air at the common pressure. The lines thus obtained, between one set of electrodes of platinum and the other of gold, were observed simultaneously; those lines common to both spectra can be measured as those due to the components of air. The spectrum thus obtained remains invariably constant, with reference to the position and relative characteristics of the lines, with all the different metals. The air-spectrum varies *as a whole*, however, in distinctness, according to the metal employed as electrodes, owing to the difference in volatility of the metals, the air in and about the electrodes being more or less replaced by the metallic vapours. The air-spectrum is made up of the spectra of the following components—nitrogen, oxygen, and hydrogen (from aqueous vapour).

The air-lines have been carefully mapped by Huggins, and are employed by him as a scale of reference for the recognition of the lines of the metals; Kirchhoff has noted on his maps only a few of the most important air-lines. Grandeau (Chem. News, ix. 66) has observed the spectrum of a flash of lightning, and, in addition to the hydrogen- and nitrogen-lines, he noticed the bright-yellow sodium-line.

Hydrogen.—The spectrum of hydrogen consists of three bright fine lines—H α (coincident with Fraunhofer's C) in the red, H β (coincident with Fraunhofer's F) in the bluish-green, and H γ in the violet. These lines are exhibited both at the ordinary and at a reduced pressure. If the rarefaction of the gas be greatly increased, the red line H α gradually disappears, whilst H β, though fainter, remains well defined. When the intensity of the spark is increased, the bands H β and H γ begin to enlarge (Plücker); and when the tension of the hydrogen is increased to 360 mm., and a Leyden-jar is introduced to raise the temperature, the bright lines are seen to have given place to a continuous spectrum. This change is never observed when the spark passes through the gas under ordinary pressure. (May this phenomenon not be due to the incandescence of the abraded solid particles of the glass of the fine thermometer-tubing, or of the platinum-electrodes?)

The hydrogen-lines may likewise be obtained by passing the spark through a vacuous tube containing a trace of aqueous vapour, the water being decomposed.

Nitrogen.—The spectrum of nitrogen, taken by a spark through air at the ordinary pressure, is a very complicated one, and especially characterised by an alternation of bright lines and dark spaces in the red, and a succession of bands in the violet. With pure nitrogen a few of the lines of the air-spectrum are wanting, but no new lines appear, and the air-lines which remain in nitrogen preserve unaltered their relative brightness and their distinctive characters. (Huggins.)

Plücker and Hittorf have made some remarkable observations on certain changes which the nitrogen-spectrum, obtained when the gas is highly rarefied, undergoes on intensifying the current. Thus, like other gases, nitrogen in the state of greatest rarefaction does not allow the induction-current to pass; but when its tension is only a fraction of a millimetre, the current begins to pass, and the gas becomes luminous. Below a certain limit of temperature, nitrogen thus ignited emits a golden-coloured light, giving a spectrum of bands; above this temperature the colour becomes bluish-violet, and a new spectrum of bands appears. If a Leyden-jar be added in the circuit, the temperature rises to a second limit, a brilliant white light is emitted, and the spectrum is again changed to one of bright lines on a dark ground; and these lines do not alter in position on further increase of temperature, though the brilliancy of all does not increase in the same ratio. Those spectra which consist of larger bands, showing various appearances from being differently shaded by fine dark lines, are called by Plücker "spectra of the first order," whereas those formed by bright lines on a dark background, or the true spectra, he terms "spectra of the second order." The nitrogen-spectrum of the second order is doubtless that of the air-spectrum. Plücker explains these differences by the assumption of several allotropic modifications of the element existing at the various temperatures.

Oxygen.—It is difficult to obtain all the lines of the oxygen-spectrum; some of them, however, have been tabulated by Huggins. Plücker, operating as with nitrogen, got only one "secondary" spectrum of oxygen, although the lines appeared to expand so as to form a continuous spectrum at the highest temperature. Huggins finds that several lines are apparently common to oxygen and nitrogen, but he regards them as due to the superposition in the air-spectrum of lines of oxygen and nitrogen.

Sulphur.—The flame of sulphur burnt in common air gives a continuous spectrum; if a small quantity of sulphur be introduced into a Geissler's tube, which is then evacuated by a Geissler's exhauster and sealed, the sulphur-spectrum is seen on passing the spark if the tube be warmed. A band-spectrum of the first order is seen at a low temperature, but this changes on continuing to heat the tube, and a spectrum of bright-coloured lines becomes visible. These two spectra are figured by Plücker and Hittorf (*loc. cit.*).

Selenium yields two spectra like sulphur.

Phosphorus, treated like sulphur, yields a spectrum of the second order. The bright lines characteristic of phosphorus are a triple line in the orange, and two bright lines in the green. These green bands may also be seen by observing the spectrum of the green spot which makes its appearance in the interior of a hydrogen-flame, when the slightest trace of a phosphorus-compound is placed in contact with the dissolving zinc. (Christofle and Beilstein, Compt. rend. lvi. 399.)

Arsenic also yields a well-defined spectrum when treated like sulphur and phosphorus.

Chlorine, bromine, and *iodine* yield spectra with bright lines, none of which are coincident. Drawings of these three spectra are given in Plücker and Hittorff's memoir.

In these cases of bodies whose spectra change from bands (first spectrum) to bright lines (second spectrum) on increase of temperature, it is found that on cooling a recombination of the elements occurs, and the spectrum of the compound reappears (Plücker). Alexander Mitscherlich (Pogg. Ann. cxxi. 459; Phil. Mag. [4], xxviii. 169) has examined the spectra of the elements and their compounds. He arrives at the conclusion (already referred to), that compounds whose vapours can be heated up to incandescence without undergoing decomposition, yield spectra different from those of their elementary constituents. The salts of the greater number of the metals (as, for instance, K, Na, Li, Mg, Zn, Cd, Hg, and Ag) decompose at so low a temperature, that the compounds of these metals always yield the metallic spectrum. Certain metallic salts (such as those of copper) require for their decomposition so high a temperature, that the true metal-spectrum can only be obtained when the solid compound is used as the electrode; whilst other compounds, such as those of calcium, strontium, and barium, are partially decomposed at the temperature of the flame of a Bunsen's gas-lamp. The spectra of the elements consist of bright lines, those of their compounds of broad bands with narrow dark spaces (see *ante*), and this division would correspond to Plücker's division of the first and second order of spectra. Mitscherlich observed (like Plücker) that iodine in the spark shows bright lines, whilst in the hydrogen-flame it exhibits broad bands; and hence he draws certain conclusions respecting the probable compound nature of this body. At present, however, we know so little of the state of combination into which bodies in the flame may enter (possible formation of hydriodic acid, for example) that such speculations seem premature. Mitscherlich has also added some singular and somewhat improbable speculations concerning a supposed relation between the atomic weights of the haloïd compounds of barium, and the distance, on an arbitrary scale, read off between the chief lines of their spectra.

Carbon.—Carbon itself, when ignited, always yields a continuous spectrum, but the spectra obtained by the combustion of the various carbon-compounds consist of complicated bright bands, and appear different from one another. Swan (Ed. Phil. Trans. xxi. 411) was the first, in 1856, to examine the lines in the spectrum of the flame of Bunsen's gas-lamp, and of the flames of many hydrocarbons. In the blue portion of the gas-flame, Swan observed four bright-blue lines, and these lines appeared in the flame of a large number of hydrocarbons, their position remaining unaffected by alteration in the composition of the burning body, either in carbon, hydrogen, or oxygen. Swan adds careful measurements of the position of these lines. Attfield (Phil. Trans. 1862, p. 221) examined the lines in the non-illuminating flames of burning hydrocarbons; he obtained similar results to Swan, but observed a larger number of lines. He attributes these lines to the glowing vapour of carbon, as all the carbon-compounds appeared to give the same spectra. Plücker and Hittorf obtained different spectra from different carbon-compounds, especially when their particles were heated in Geissler's tubes. They found that all the lines obtained by all the various carbon-compounds existed in the cyanogen-spectrum, but they express themselves unable to explain fully the various types of spectra of carbon. Dibbits (Pogg. Ann. cxxii. 497) also found a remarkable difference between the spectrum of a hydrocarbon and that of cyanogen burning in oxygen.

The flame issuing from the Bessemer-steel converter, and especially that seen when the specular iron is poured into the molten iron, exhibits the carbon-lines most vividly (Roscoe). Huggins has observed, that when air contains some quantity of carbonic anhydride, several new lines are seen in the air-spectrum, and these coincide with the spectrum of graphite; one of the strongest and most characteristic of these is a red line, rather less refrangible than the hydrogen-line, and this may be used as a test of the presence of carbonic anhydride.

Solar and Stellar Chemistry.

unhofer, in 1814, examined the relative positions of the dark lines observed in
e Moon and Venus (reflected sunlight), and found that in the spectra of
of light, the dark lines were identical in number and position with
spectrum. Fraunhofer saw in Venus-light the double D lines,
and the relative distance from D to E and from E to F was
in the Solar spectrum. He also examined the light given
d stars (Sirius for instance), and found that lines or bands

were present which do not exist in sunlight, direct or reflected. Amongst the lines of Procyon, Fraunhofer recognised the solar line D, and in those of Capella and Betalgeux he found both D and *b*, but all the stellar spectra differed in certain respects from that of sunlight. Hence Fraunhofer concluded that the lines which we notice in the solar spectrum are, in some way or other, produced in the sun. Fraunhofer made another important observation—viz., that of the exact coincidence of the bright sodium-line, Na *α*, with the dark double solar line D. These early observations of Fraunhofer have lately been confirmed by Miller and Huggins (Phil. Trans. 1864, p. 418). It was, however, reserved for Kirchhoff (Monatsber. d. Berlin. Acad. Oct. 20, 1859) definitively to explain this coincidence, and thereby to obtain a key to the determination of the chemical composition of the sun and stars.

The Reversal of the Spectra of Coloured Flames.

In the year 1849 Foucault (Institut. 1849, p. 45) observing the spectrum of the electric arc, and comparing it with the solar spectrum, found that in both spectra the dark double line D was seen, the bright (sodium) lines present being changed into dark bands in the spectrum produced by the light from one of the carbon-poles which had been allowed to pass through the luminous arc. This experiment was in no way explained, nor did it attract much attention at the time, and it was unknown to Kirchhoff and Bunsen when they began their researches in 1859.

The mode in which Kirchhoff first obtained the true explanation of this important point cannot be given more concisely and clearly than in his own words (*Researches*, part i. p. 13): "In order to test, by direct experiment, the truth of the frequently asserted fact of the coincidence of the sodium-lines with the lines D, I obtained a tolerably bright solar spectrum, and brought a flame coloured by sodium-vapour in front of the slit. I then saw the dark lines D change into bright ones. The flame of a Bunsen's lamp threw the bright sodium-lines upon the solar spectrum with unexpected brilliancy. In order to find out the extent to which the intensity of the solar spectrum could be increased, without impairing the distinctness of the sodium-lines, I allowed the full sunlight to shine through the sodium-flame upon the slit, and, to my astonishment, I saw that the dark lines D appeared with an extraordinary degree of clearness. I then exchanged the sunlight for the Drummond's light, giving a continuous spectrum. When this light was allowed to fall through a suitable flame coloured by common salt, dark lines were seen in the spectrum in the position of the sodium-lines. The same phenomenon was observed if, instead of the incandescent lime, a platinum-wire was used, which, being heated in a flame, was brought to a temperature near to its melting-point by passing an electric current through it.

"The phenomenon in question is easily explained upon the supposition that the sodium-flame absorbs rays of the same degree of refrangibility as those it emits, whilst it is perfectly transparent for all other rays. This supposition is rendered probable by the fact, which has long been known, that certain gases, as nitrous acid and iodine-vapour, possess at low temperatures the property of such a selective absorption. The following considerations show that this is the true explanation of the phenomenon. If a sodium-flame be held before an incandescent platinum-wire whose spectrum is being examined, the brightness of the light in the neighbourhood of the sodium-lines would, according to the above supposition, *not* be altered; in the position of the sodium-lines themselves, however, the brightness *is* altered, for two reasons: in the first place, the intensity of the light emitted by the platinum-wire is reduced to a certain fraction of its original amount by absorption in the flame, and secondly, the light of the flame itself is added to that from the wire. It is plain that if the platinum-wire emits a sufficient amount of light, the loss of light occasioned by absorption in the flame must be greater than the gain of light from the luminosity of the flame: the sodium-lines must then appear darker than the surrounding parts, and, by contrast with the neighbouring parts, they may seem to be quite black, although their degree of luminosity is necessarily greater than that which the sodium-flame alone would have produced. The absorptive power of sodium-vapour becomes most apparent when its luminosity is smallest, or when its temperature is lowest."

If the spectrum emitted by a piece of sodium burning in the air be examined, the true sodium-spectrum will be seen to be reversed, exhibiting two dark lines (D) on a background of a continuous spectrum. Here the solid particles of soda give the continuous spectrum, and the sodium-vapour absorbs a great portion of the yellow rays. This can be well shown to an audience, and the black absorption-band projected on a screen, by placing a small piece of sodium on the lower carbon in the electric lamp; by approaching and separating the poles, this black line can be made alternately to appear and disappear for the space of several minutes. Another mode of showing that sodium-vapour is opaque to the light which it emits, is to burn a small jet of hydrogen, in which two soda-beads are placed, in front of a large sheet of flame rendered yellow by burning a piece of sodium near it. If the small flame be now looked at projected on a background of the large yellow flame, the hydrogen-flame appears surrounded by a dark zone, as if it smoked; this is due to the absorption of the yellow light of the large flame, by the vapour of sodium at the outside of the small flame (Crookes). A second method of showing this same property is to seal up some sodium in a vacuous tube; on volatilising the sodium, the vapour of the metal appears colourless by white light, but is dark and opaque when illuminated by the yellow soda-flame. (Roscoe).

Kirchhoff has, in like manner, reversed the red lithium-line Li α; if direct sunlight be allowed to pass through a lithium-flame, the spectrum exhibits, in place of the red lithium-line, a black line, which in distinctness bears comparison with the most remarkable of Fraunhofer's lines, and disappears when the flame is withdrawn. The bright lines of potassium, strontium, calcium, and barium (Kirchhoff and Bunsen), and some of the blue lines in the copper-spectrum (W. A. Miller) have also been *reversed*.

Kirchhoff has added to these discoveries a mathematical treatment of the proposition upon which the phenomena are based (*Ueber den Zusammenhang zwischen Emission und Absorption von Licht und Wärme*, 15 Dec. 1859, Monatsberichte d. Berliner Acad., and Phil. Mag. March 1860). This principle is known as the "Theory of Exchanges," and may be thus expressed: "The relation between the power of emission and power of absorption, for each kind of rays (light or heat), is the same for all bodies at the same temperature. From this proposition it follows that a glowing body which emits only rays of certain wave-lengths likewise absorbs only rays of the same wave-lengths; and from this we learn how the dark lines in the solar spectrum reveal the constituents of the sun's atmosphere." This definite relation, which exists between the radiating and absorbing powers of bodies for definite descriptions of light and heat, is thus clearly expressed by Kirchhoff:

"Let R denote the intensity of radiation of a particle for a given description of light at a given temperature, and let A denote the proportion of rays of this description incident on the particle which it absorbs; then $\frac{R}{A}$ has the same value for all bodies at the same temperature—that is to say, this quotient is a function of the temperature only."

Other physicists had previously approached very close to the "Theory of Exchanges," as expressed by Kirchhoff; thus Balfour Stewart, in 1858 (Trans. Roy. Soc. Edin.), enunciated this principle completely for the heating rays, which indeed had previously been proposed, first by Prevost, and afterwards by Provostaye and Desains. Stewart afterwards (Feb. 1860), applied this theory to the luminous rays, but his publication was later than, although independent of Kirchhoff's. Angström, especially, came near to Kirchhoff's discovery; in his *Optischen Untersuchengen* (Phil. Mag. ix. 329), he states the proposition that a body "in the state of incandescence must emit exactly all those kinds of light which it absorbs at the common temperature." In his further development of the subject there appear to be some contradictions, but he concludes by saying that—"I am convinced that the explanation of the dark lines in the solar spectrum embraces that of the luminous lines in the electric spectrum."

Stokes and William Thomson (Phil. Mag. 1862, p. 158) seem also to have expressed in conversation (although not to have published), the true explanation of the cause of the dark D lines, for some years before Kirchhoff's publication; but still, the experimental verification and scientific proof were wanting, until the latter physicist gave it, partly by his theoretical considerations, and partly by the experiments above referred to. (See Balfour Stewart, *Report on the Theory of Exchanges*, Brit. Assoc. 1861.—Kirchhoff, *On the History of Analysis of the Solar Atmosphere*, Phil. Mag. [4] xxv. 250.—B. Stewart, *Reply to Kirchhoff's Paper on the History*, &c. Phil. Mag. [4], May 1863.)

Euler was the first to predict the existence of the Law of Exchanges, by assuming, as a fundamental principle, that a body absorbs all the series of oscillations which it can itself assume. Stokes (Phil. Mag. 1860), in commenting on Kirchhoff's discovery, illustrates the principle by a dynamical example concerning sound, in which the well-known phenomenon of resonance is the equivalent to the emission and absorption of light.

On the Coincidence of the Bright Rays of certain Metals with the Dark Lines in the Solar Spectrum, and the Existence of certain Metals in the Solar Atmosphere.

The coincidence of the yellow soda-lines with the dark D line was observed by Fraunhofer, and Kirchhoff having discovered the phenomenon of the reversal of the bright lines, concluded that sodium-vapour is present in the solar atmosphere. In order to determine with certainty whether the bright lines of any other metal were coincident with solar lines, Kirchhoff mapped the solar lines with great care, and compared their position with the bright metal lines. *Fig.* 773 gives a representation of his drawings of a very small portion of the spectrum between *b* and F, showing the coincidences of many metallic lines. In thus examining the two spectra, Kirchhoff found that dark lines occur in the solar spectrum in the positions of all (about 80) the bright iron lines, and he believes that each of the coincidences thus observed may be at least as well established as that of the sodium-lines with the D line was up to the present time. Kirchhoff proceeds to calculate, from the average distance between each of the lines, and their number, the probability that this coincidence is a mere work of chance; this he finds to be less than $(\frac{1}{2})^{60}$, or less than $\frac{1}{1,000,000,000,000,000,000}$.

This probability is increased by the fact that the brighter a given iron line is seen to be, the darker, as a rule, does the corresponding solar line appear. Hence this coincidence must be produced by some cause, and a cause can be assigned which affords a perfect explanation of the phenomena. It is explained, if we suppose that the rays of light which we thus examine have at one time been rays of all degrees of refrangibility, such as we get from the Drummond's light; that this light has passed through the vapour of iron; and that this iron-vapour, absorbing exactly the same kind of light which it is capable of emitting, produces the dark lines which we observe. The vapour of iron causing these dark lines, may be present either in our own atmosphere, or in that of the sun. It is, however, very unlikely that there can be sufficient iron-vapour in our atmosphere to effect this alteration, and we observe that the starlight also passing through our atmosphere differs essentially from sunlight; whilst, on the other hand, it does not seem unlikely, owing to the high temperature which we must suppose the sun's atmosphere to possess, that such vapours should be present in it. "Hence," says Kirchhoff, "the observations of the solar spectrum appear to me to prove the presence of iron-vapour in the solar atmosphere, with as great a degree of certainty as we can attain in any question of natural science."

As soon as the existence in the solar atmosphere of one terrestrial element has been discovered, the comparison of the spectra of other metals is immediately suggested, as it is reasonable to suppose that other bodies well known on this earth may in like manner be found to be present in the sun. In this way, coincidences were found to exist between the solar lines and those of the following metals; and although the number of these coincidences for each of these metals is smaller than was observed with iron, yet they are so characteristic and distinct, as to leave no doubt of the presence of these metals in the solar atmosphere:—

1. Sodium.
2. Calcium.
3. Barium.
4. Magnesium.
5. Iron.
6. Chromium.
7. Nickel.
8. Copper.
9. Zinc.
10. Strontium.
11. Cadmium.
12. Cobalt.
13. Hydrogen.

There is some degree of doubt about strontium, cadmium, and cobalt, either because only a few coincidences have been observed, or because one or more prominent metal lines have no dark representative in the solar spectrum. The following elements appear to be absent from the solar atmosphere:—

1. Gold.
2. Silver.
3. Mercury.
4. Aluminium.*
5. Rubidium.
6. Tin.
7. Potassium.
8. Lead.
9. Antimony.
10. Arsenic.
11. Lithium.
12. Silicium.
13. Glucinum.
14. Cerium.
15. Lanthanum.
16. Didymium.
17. Ruthenium.
18. Iridium.
19. Palladium.
20. Platinum.

Hydrogen has been shown by Angström and Plücker to be present in the sun's atmosphere. The cause of many of the best-known of the Fraunhofer's lines has thus been already ascertained:

The line C is caused by hydrogen (Angström).
" " D " " sodium (Kirchhoff).
" " E " " iron "
" " C " " magnesium "
" " F and G " hydrogen "
" " H " " aluminium (Angström).

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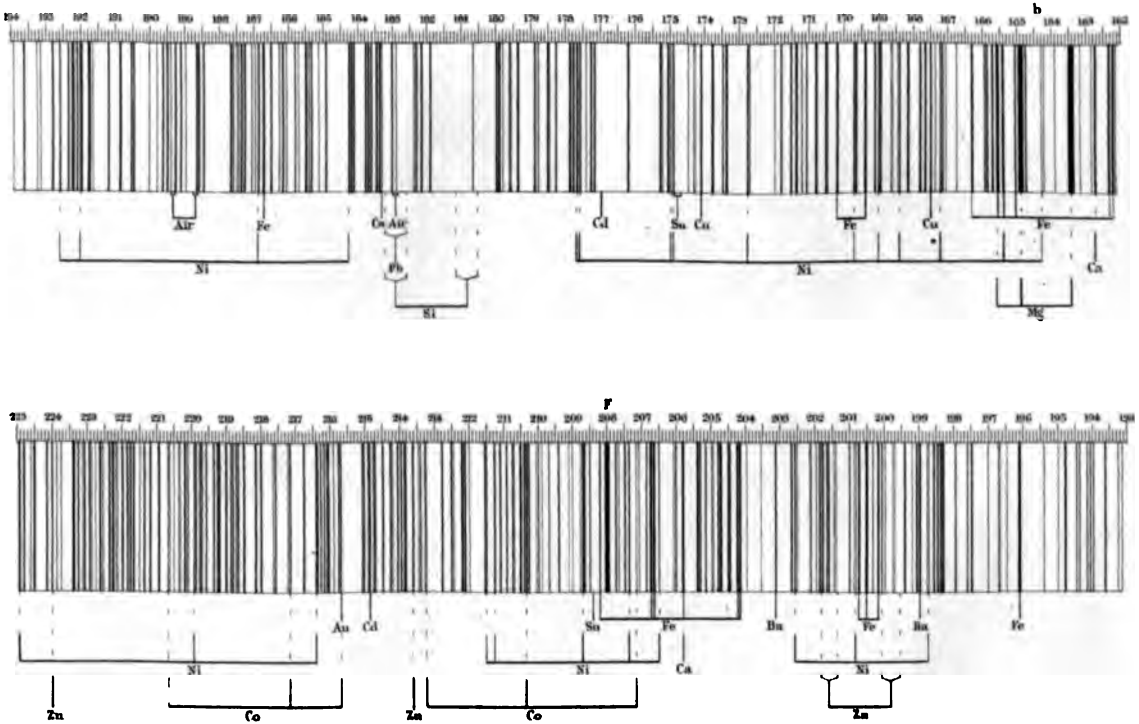
* According to Angström, a line of aluminium corresponds to Fraunhofer's H. Kirchhoff's maps do not extend so far as this.

b
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It is not, however, to be supposed that the whole of the dark lines are produced by absorption in the solar atmosphere; there are certain lines or bands which are doubtless produced by absorption in our own atmosphere. This is ascertained by the fact, that these bands increase in darkness, and new ones become apparent when the sun approaches the horizon, and the light has to pass through a deeper column of air. These air-absorption lines have been studied, and many of them mapped, by Brewster and Gladstone (Phil. Trans. 1860, p. 149). Several have also been mapped by Hofmann, and described in Kirchhoff's second memoir; of these some were found to be coincident with the brightest lines of the air-spectrum, obtained with the spark.

The increase or otherwise of these atmospheric absorption-lines has been applied by Huggins and Miller (Phil. Trans. 1864, p. 420) to the investigation of the question as to the existence of a lunar atmosphere; not the smallest change could be observed in the lines of the spectrum, either as respects relative intensity, or in the addition or disappearance of any lines when the moon's spectrum was examined. Hence the result of the spectrum-analysis of the light reflected by the moon is wholly negative as to the existence of any considerable lunar atmosphere. The light reflected from Jupiter exhibits, on the other hand, a distinct difference, especially from direct sunlight, inasmuch as, especially, one band in the red is seen to appear in light reflected from this planet. Hence spectrum-analysis confirms astronomical observation in the conclusion that Jupiter possesses an atmosphere of considerable density. Some of the lines in Saturn-light, although much weaker, appear to be the same as those seen in the spectrum of Jupiter. Mars does not exhibit the lines characteristic of the atmosphere of Jupiter and Saturn; groups of lines appear in the blue portion of the spectrum, and these, by causing the predominance of the red rays, may be the cause of the red colour which distinguishes the light of this planet. Venus showed no additional lines.

In the case of most of the planets, the solar light is probably reflected, not from the planetary surface, but from clouds at some elevation above it; under such circumstances, the light would not be subjected to the absorbent action of the lower and denser portions of the planet's atmosphere; and it is precisely these in our atmosphere, which are most effectual in producing the so-called atmospheric lines. (Huggins.)

M. Janssen has lately (Compt. rend. lvi. 538; lx. 213) obtained the complete absorption-spectrum of aqueous vapour, by passing the rays from a gas-flame through a tube 40 metres long filled with high-pressure steam. He has observed the coincidence of a very large number of these aqueous lines with lines observed in the solar spectrum, especially when the sun's altitude is low; and hence he has proved that these atmospheric lines are due to the presence of aqueous vapour. Janssen has also observed the existence of these lines in light reflected from Jupiter and Saturn, and hence it appears very probable that the atmospheres of these planets contain aqueous vapour.

A most interesting confirmation of the accuracy of Kirchhoff's drawings of the dark lines has recently been made by Rutherford of New York, who has succeeded in obtaining most exact photographs of the solar spectrum, on a scale nearly equal to that of the drawings; and on comparing the two, the correspondence of line for line is so complete, that it requires a close examination to detect differences which, however, are visible on careful inspection.

For details concerning the physical constitution of the sun, we must refer the reader to the original memoirs, as the questions at issue become purely physical and astronomical. The following extract from Kirchhoff's first memoir must suffice as giving his views on the subject:—

"In order to explain the occurrence of the dark lines in the solar spectrum, we must assume that the solar atmosphere encloses a luminous nucleus producing a continuous spectrum, the brightness of which exceeds a certain limit. The most probable supposition that can be made respecting the sun's constitution, is that it consists of a solid or liquid nucleus, heated to a temperature of the brightest whiteness, surrounded by an atmosphere of a somewhat lower temperature. This supposition is in accordance with Laplace's celebrated nebular hypothesis respecting the formation of our planetary system. If the matter now concentrated in the several heavenly bodies existed in former times as an extended and continuous mass of vapour, by the contraction of which sun, planets, and stars have been formed, all these bodies must necessarily possess mainly the same constitution. Geology teaches us that the earth once existed in a state of fusion; and we are compelled to admit that the same state of things has occurred in the other members of our solar system. The amount of cooling which the various heavenly bodies have undergone, in accordance with the laws of the radiation of heat, differs greatly, mainly owing to difference in their masses. Thus, whilst the moon has become cooler than the earth, the temperature of the sun has not yet sunk below a white heat. Our terrestrial atmosphere, in which now so few elements are found, must have possessed, when the earth was in a state of fusion, a much more complicated composition, as it then contained all those substances which are volatile at a white heat. The solar atmosphere at present possesses such a constitution."

[On the physical constitution of the sun, see "The Heavens," by Guillemin and Lockyer (Bentley, 1866), p. 17, &c.; Brayley, in Companion to the Almanac for 1864 and 1865; Memoirs by Carrington and by De la Rue, Stewart, and Loewy.]

Stellar Chemistry.

It has already been stated, that Fraunhofer was aware that the star-spectra differed from the spectra of the sun, moon, or planets. In 1862 Donati published diagrams of three or four lines in fifteen stars (*Intorno alle strie degli spettri stellari*, Il Nuovo Cimento, xv. 292), but the position of these lines did not correspond with Fraunhofer's results. In February 1863, Huggins and W. A. Miller communicated to the Royal Society some measurements of the lines in Sirius, Aldebaran, and α Orionis, whilst Rutherford about the same time made similar observations (Sill. Am. Journ. xxxv. 71). Secchi (Astronomische Nachrichten, 3. März 1863) also measured a few lines, as also did the Astronomer Royal (Monthly Notices, xxiii. 190). By far the most complete and accurate investigation of the stellar spectra is that by Huggins and W. A. Miller (Phil. Trans. 1864, p. 413). The investigation was carried on at Mr. Huggins's observatory, and the spectroscope, containing two prisms having each a refracting angle of 60°, is fixed to an 8-inch refracting telescope by Alvan Clarke.

In order to obtain evidence of the presence of dark lines in the stellar spectrum, the line of light obtained as the spectrum of the luminous point required to be spread out to a band; this was effected by a cylindrical lens placed within the focus of the object-glass, and immediately in front of the slit of the collimator of the spectroscope. The apparatus, when adjusted, is powerful enough to show the fine nickel line within the double D line in the solar spectrum. A micrometer movement is attached to the spectroscope, by which the position of the lines can be determined to within the $\frac{1}{2000}$ part of the distance of A to H.

Such measurements are, however, not sufficient to determine the chemical constitution of the stellar atmosphere; this can only be done by direct comparison with the metallic spectra, and hence arrangements were made for throwing the light from a flame or from the electric spark into the instrument, so that the two spectra are seen at once.

The following gives the results of careful comparison of the spectra of Aldebaran and Betelgeux (α Orionis) with bright lines of the metals:

ALDEBARAN.

Coincident Elements.		
1. Hydrogen	with	lines C and F.
2. Sodium	,,	double line D.
3. Magnesium	,,	triple line b.
4. Calcium	,,	four lines.
5. Iron	,,	four lines and E.
6. Bismuth	,,	four lines.
7. Tellurium	,,	four lines.
8. Antimony	,,	three lines.
9. Mercury.	,,	four lines.

Non-coincident Elements.		
Nitrogen	with	three lines.
Cobalt	,,	two lines.
Tin	,,	five lines.
Lead	,,	two lines.
Cadmium	,,	three lines.
Barium	,,	two lines.
Lithium	,,	one line.

Seventy lines measured.

BETELGEUX (α ORIONIS).

Coincident Elements.		
1. Sodium	with	double line D.
2. Magnesium	,,	triple line b.
3. Calcium	,,	four lines.
4. Iron	,,	three lines and E.
5. Bismuth	,,	four lines.
6. Thallium (?)		

Non-coincident Elements.		
Hydrogen	with	C and F
Nitrogen	,,	three lines.

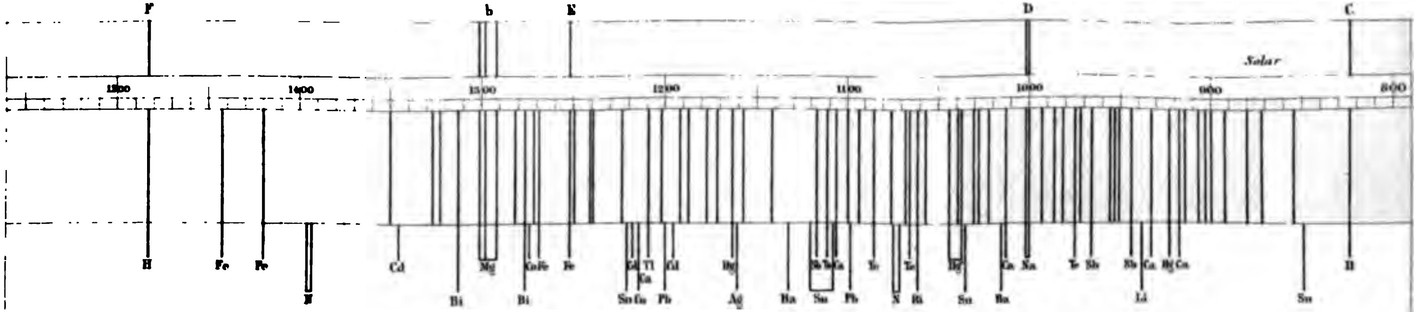
Non-coincident Elements (cont.)		
Tin	with	five lines.
Lead	,,	two lines
Gold(?)		
Cadmium	,,	three lines
Silver	,,	two lines.
Mercury	,,	four lines.
Barium	,,	two lines.
Lithium	,,	one line.

Eighty lines measured.

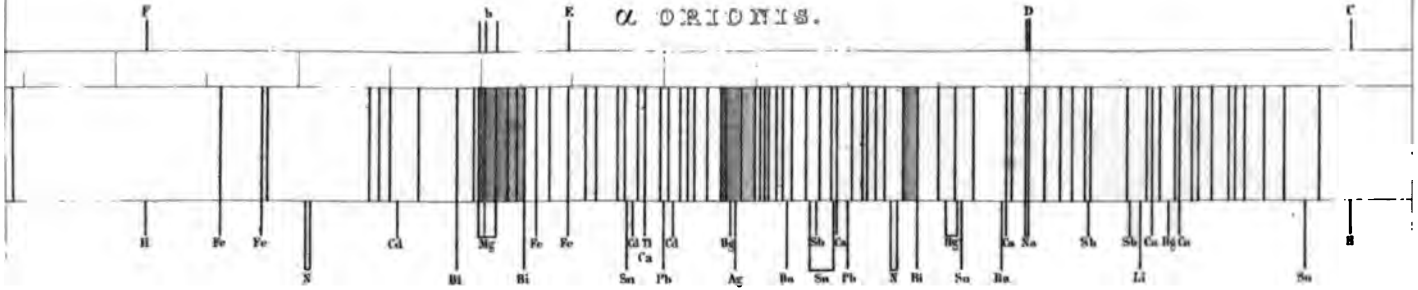
Fig. 774 is a copy of Huggins and Miller's drawing of the spectra of Aldebaran and of Betelgeux (half original size).

The seventy or eighty lines measured indicate only some of the stronger of the numerous lines which are seen in the spectra of these stars. "Some of these are probably due to the vapours of other terrestrial elements which have not been compared with these stars. It would be assumption to suppose that the sixty-five so-called elements constitute the entire primary material of the universe. Doubtless in the

ALDEBARAN.



α ORIONIS.



Longmans & C°

spectra of the stars the chemist is introduced to many new elements—would that it were possible for him to recognise and to isolate them!" (Huggins.)

In only two out of fifty stars examined were the lines of hydrogen, C and F, found absent; these are α Orionis and β Pegasi:

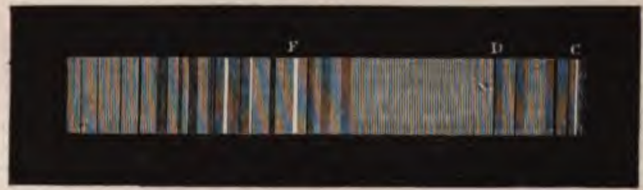
β Pegasi	contains	sodium,	magnesium,	perhaps barium.	
Sirius	,,	,,	,,	iron,	hydrogen.
α Lyræ (Vega)	,,	,,	,,	,,	,,
Pollux	,,	,,	,,	,,	,,

All the stars which have been examined yield spectra containing dark lines, star differing from star only in the grouping and arrangement of the numerous fine lines which cross their spectra. Hence the physical constitution of the fixed stars resembles that of our sun; the source of their light is solid or liquid matter in a state of incandescence, and this nucleus is surrounded by an atmosphere of the vapours of such of the elements of the star as are volatile at their high temperature. The results already obtained respecting the chemical composition of stellar atmospheres have an interesting bearing upon Laplace's nebular theory, as these results appear to show that the visible universe is composed mainly of the same elementary constituents, many of those known on this earth being found in the far-distant stars.

These spectrum-observations also lead to the presumption, that the well-known difference in colour observed in the stars may be caused by a difference in the chemical constitution of the stellar atmospheres, causing a variation in the absorption of the white light of the nucleus, and thus giving a difference in the colour to the starlight as seen by us.

One of the most interesting and extraordinary of astronomical observations ever made with respect to the stars has lately been described by Huggins and Miller (Proc. Roy. Soc. xv. 146, May 17, 1866). On the evening of May 15, Mr. Baxendell, of Manchester (an authority on variable stars), observed a new star. "This," he says, "suddenly burst forth in Corona. It is somewhat less than a degree distant from E of that constellation in a south-easterly direction, and last night (May 15) was fully equal in brilliancy to β Serpentis or ν Hercules, both of the third magnitude;" and Mr. Baxendell describes the star as exhibiting a nebulosity, "as if the yellow of the star were seen through an overlying film of a blue tint." On examining the light of the star, Huggins found that its spectrum was unlike that of any celestial body hitherto examined. The light of the star is compound, and has emanated, as Baxendell surmised, from two sources. Each light forms its own spectrum, and these two spectra appear superposed in the telescope. The chief spectrum is analogous to that of the sun, consisting of dark lines on a bright background, caused by light from a glowing nucleus passing through an absorbing atmosphere; the second spectrum consists of a few bright lines, indicating that the light is formed by matter in the condition of incandescent gas. The spectrum of this star is represented in *fig.* 775.

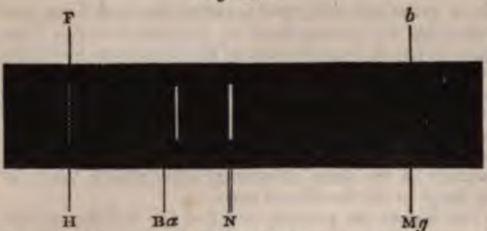
Fig. 775.



The brightest of the bright bands coincided with Fraunhofer's F, and therefore with the blue hydrogen-band; on account of the faintness of the red end of the spectrum, the coincidence of the red band with the red hydrogen-line could not be determined with equal certainty, though it is probable. The physical constitution of the star, as thus seen, must be very remarkable; it must consist of a solid nucleus and gaseous atmosphere, like an ordinary star, together with a separate outburst of ignited gas (probably hydrogen). The luminosity of the star quickly diminished, and on May 24 it had become as low as the eighth magnitude; the bright bands were seen gradually to disappear, whilst the other spectrum remained. Hence the bold speculation suggests itself that large quantities of gas have been evolved by some vast convulsion; that this gas (hydrogen), by burning, was heated to incandescence, and that this heated the whole solid matter and photosphere of the star, but that, as the hydrogen becomes exhausted, all the phenomena diminish in intensity, and the star rapidly wanes.

Spectra of the Nebulæ (Huggins, Phil. Trans. 1864, p. 437).—The special examination of the bodies known as planetary nebulæ has proved that their constitution is totally different from that of sun, planets, and fixed stars. They are all found to yield a spectrum consisting entirely of *bright* lines, without any continuous spectrum. Thus a bright nebula in Draco (No. 4373) gave, on careful examination, a spectrum consisting of one bright line coincident with the brightest of the air (nitrogen) lines, a second less brilliant line nearly coincident with a green barium-band, and a third still more refrangible line very much fainter, and coincident with one of the hydrogen-lines, viz. F of Fraunhofer; a very faint and scarcely visible continuous spectrum was just perceived on each side of the group of bright lines, due probably to the solid or liquid matter of the nucleus, which in this nebula is visible by its greater luminosity in the centre. A second bright nebula in Taurus Poniatowskii (No. 4390) exhibited the same spectrum as the last-mentioned nebulæ, and six other nebulæ showed either some or all of these same three lines. Of the sixty nebulæ examined by Huggins, about one-third exhibited these bright lines, whilst about forty, when spread out by the prism, yielded spectra apparently continuous. It is evident, from these observations, that many of the nebulæ can no longer be regarded as aggregations of suns, after the order to which our own sun and the fixed stars belong. We have in these objects no longer to do with a special modification only of our own type of suns, but find ourselves in the presence of objects possessing a distinct and peculiar plan of structure (Huggins). A question of great interest next presented itself—viz., do those nebulæ, which have certainly been resolved by the telescope into star-clusters, exhibit a spectrum which shows the source of light to be glowing gas? For this purpose Huggins examined the celebrated nebula in the sword-handle of Orion (Proc. Roy. Soc. 1865, p. 39). The light from the brightest part of the nebula, near the trapezium, was resolved by the prisms into three bright lines, similar in all respects to those of the other gaseous nebulæ. When the stars of the trapezium were brought into the slit, a continuous spectrum was at once seen; but the whole of the nebula emits the same kind of light, differing only in intensity. Thus, whilst the evidence afforded by the largest telescopes appears to be that the brighter parts of this nebula consist of a "mass of stars," the conclusions drawn from a prismatic analysis of the light, is that these luminous points are not stars, but masses of gaseous matter. Conclusions respecting the distance of these nebulæ, founded upon the erroneous supposition that they consist of stellar masses, must therefore be given up, as far at least as concerns the nebulæ which are proved to be gaseous.

Fig. 776.



Comets.—The light of comets has not escaped the searching investigation of Huggins's spectroscope (Proc. Roy. Soc. xv. 5; Jan. 1866). He finds that the spectrum of Comet I. 1866 consists of a broad continuous spectrum, with a bright point about midway between *b* and F in the solar spectrum, and coincident with the bright nitrogen-line observed in many nebulæ. Hence we learn that the light from the coma of this comet is different from that of its nucleus. The nucleus is self-luminous, and the matter of which it consists is in the state of ignited gas. As we cannot suppose the coma to consist of incandescent solid matter, the continuous spectrum probably indicates that it shines by reflected sunlight, and this appears to be in accordance with observations on the polarisation of light in the tails of some comets. (Bond.)

Meteors.—Mr. Alexander Herschel has recently succeeded in observing the spectrum of a bright meteor, and also the spectra of some of the trains which meteors leave behind them. A remarkable result of his observations is, that sodium exists in the state of luminous vapour in the trains of most meteors.

The results of the examination of the spectra of the stellar bodies may be shortly summed up in the words of Mr. Huggins (Lecture at Nottingham Meeting of the British Assoc. 1866):

1. All the brighter stars, at least, have a structure analogous to that of the sun.
2. The stars contain material elements common to the earth and sun.
3. The colours of the stars have their origin in the chemical constitution of the atmospheres which surround them.

4. The changes in brightness of some of the variable stars are attended with changes in the lines of absorption of their spectra.

5. The phenomena of the star in Corona appear to show that in this object at least, great physical changes are in operation.

6. There exist in the heavens *true nebulæ*. These objects consist of luminous gas.

7. The material of comets is very similar to the matter of gaseous nebulæ, and may be identical with it.

8. The bright points of the star-clusters may not be in all cases stars of the same order as the separate bright stars. H. E. R.

SPECULAR IRON. Syn. with red hæmatite, or native ferric oxide (iii. 338, 339).

SPECULUM METAL. An alloy of tin and copper, with a small proportion of arsenic, sometimes also containing zinc. (See COPPER, ALLOYS OF, ii. 44.)

SPEISS. A mixture of the sulphides, arsenides, or antimonides of nickel, iron, and copper, which collects at the bottom of the pot when ores of cobalt or lead, containing sulphur and arsenic or antimony, are melted with fluxes. The term is applied chiefly to the nickeliferous product which is obtained in the preparation of smalt (p. 313), and used as a source of nickel.

SPELTER. A commercial name of zinc.

SPERMACETI. The fatty substance found in peculiar cavities in the head of the sperm-whale (*Physeter macrocephalus*), also of *Ph. Tursio* and others, and of the *Delphinus edentulus*, being kept in solution in the sperm-oil by the heat of the animal's body, and crystallising out after death. It is freed as much as possible from oil by filtration and by treatment with potash-ley, and then melted. The fused and solidified mass, constituting the spermaceti of commerce, is white, scaly, brittle, soft to the touch, of specific gravity 0·943 at 15° (0·843 at 50°, 0·824 at 81°, 0·813 at 94°, the specific gravity of water at 15° being taken as 1—Saussure); melting-point from 38° to 47°; neutral, inodorous, and nearly tasteless.

Spermaceti is also found in small quantity in the blubber of the *Balæna rostrata* (Scharling, J. pr. Chem. xliii. 257), and, with but slightly different properties, in the oil of *Delphinus globiceps*. (Chevreul.)

When spermaceti is freed from adhering sperm-oil by means of cold alcohol, and the residue repeatedly crystallised from hot alcohol, the spermaceti-fat (or *cetin* of Chevreul) is obtained. This may be still further purified by crystallisation from boiling ether (i. 838).

SPERM-OIL. This oil occurs, together with spermaceti—from which it is separated by mechanical means—in the head of *Physeter macrocephalus*, &c.

When freed as completely as possible from admixed spermaceti-fat, by leaving the latter to crystallise out, it is neutral, remains liquid at 18°, is saponified with difficulty by potash, and yields by that process the same fatty acids as spermaceti-fat; but instead of ethal, a neutral product melting at 23° (Chevreul, *Recherches*, p. 237). Sperm-oil appears to be isomeric with spermaceti-fat or cetin (Stenhouse).—The oil which runs off from the spermaceti-fat solidifies almost completely at 0°, to a compact light-brown mass, in consequence of still retaining spermaceti-fat. When saponified it gives off ammonia, with traces of methylamine, and yields physetoleic acid (iv. 634), valerianic acid, small quantities of solid fatty acids, with a small quantity of glycerin. (Hofstädter.)

SPERMATIC FLUID. The sexual secretion of the male, supplied mainly by the *testes*, but receiving some of its constituents from other glands (*prostate*, &c.)—a ropy, whitish, neutral or faintly alkaline fluid, of a peculiar odour. It contains remarkable minute locomotive bodies called *spermatozoa* (the essential agents of fecundation), swimming, together with sperm-corpuscles, mucus-corpuscles, and epithelium-scales, in an albuminous medium. The spermatozoa, which are but very slowly affected by processes of decomposition, and whose movements are variously modified by saline solutions of various degrees of concentration, and by other chemical agents, are rich in protagon, and appear to be composed, in part at least, of some albuminoïd substance; but they offer great resistance to reagents, and lose their outlines only in warm concentrated solutions of caustic alkalis. The fluid in which they swim contains an albuminoïd matter, resembling to some extent both mucin and casein, to which the name of *spermatin* has been given. It is coagulated by alcohol, but not by heat; acetic acid produces a precipitate which is soluble in an excess of the reagent, but can be reprecipitated from the acid solution by ferrocyanide of potassium. Spermatin when dried becomes insoluble in water, but soluble in dilute alkalis, from which it may be precipitated by the addition of concentrated solutions of the alkaline carbonates.

Spermatic fluid is rich in salts, especially in earthy phosphates; crystals of triple phosphate very speedily appear in decomposing specimens. According to **Köllicker**, 100 parts of the spermatic fluid of the ox contain 17·94 solid matters, of which 15·3 are albuminoïd and extractives, 2·16 fat, and 2·637 salts. The secretion of the prostate of the dog contains, according to **Buxmann** (Henle und Meissner's Bericht, 1864, p. 286) 98·5 per cent. of water, 4·5 per cent., and nearly 1 per cent. of chloride of sodium, together with small quantities of sulphate and phosphate of potassium and calcium. M. F.

SPESSARTIN. Manganese garnet (ii. 772).

SPHÆRIA DEUSTA. This fungus yields (? air-dried) 6·5 per cent. of an alkaline ash, containing ferric oxide and a large quantity of silica. Moderately dilute hydrochloric acid extracts from the plant about half its fixed constituents, leaving a dark-brown or black residue, which withstands the action of all concentrated mineral acids (except nitric acid), imparts only a slight colour to boiling potash-ley, and yields (dried at 120°, and calculated upon the substance free from ash), 61·6 per cent. C, 4·0 H, 1·2 N, and 33·2 O. The fungus yields, by dry distillation, an acid fetid distillate. (A. and W. **Knop**, Pharm. Centr. 1851, p. 648.)

SPHÆROCOCCUS LICHENOÏDES. According to **Gonnermann** and **Ludwig** (Arch. Pharm. [2] cxi. 204), this alga (from Ceylon) contains in its cells true starch-grains, which are at first coloured yellowish by iodine, and turn blue only on warming.

SPHAGNUM. A club-moss which grows chiefly on peat-moors, and often plays an essential part in their formation. *Sph. acutifolium* contains, according to C. **Sprengel** (J. techn. Chem. xv. 32), 3·05 per cent. ash (*a*); according to **Vohl**, (Ann. Ch. Pharm. cix. 185), the same from a high moor in the Canton of Zurich contains 0·92 per cent. of ash (*b*); and *Sph. cuspidatum*, from Upper Bavaria, contains, according to **Wittstein** (Jahresb. 1862, p. 510), 2·014 per cent. ash, composed of—

	K^2O.	Na^2O.	CaO.	MgO.	Al^2O^3.	Fe^2O^3.	SO^3.	P^2O^5.	SiO^2.	CO^2.	Cl.	NaCl.	
Sph. acutifolium (*a*).	10·9	13·9	. .	5·8	3·4	7·0	4·0	. .	43·8	. .	11·2	. .	= 100
„ „ (*b*).	8·02	1·84	3·17	4·92	5·89	6·35*	4·33	1·06	41·69	. .	. .	19·92	= 97·19
„ *cuspidatum*.	4·89	6·37	14·06	3·02	2·84	10·35	3·16	2·79	39·92	6·97	. .	4·96	= 99·33

SPHALERITE. Syn. with Blende. (See Zinc.)

SPHENE. A calcic silico-titanate, occurring in monoclinic crystals having the axis $a : b : c = 1·326 : 1 : 0·5678$; angle of inclined axes $(b, c) = 60° 27'$; $\infty P : \infty P = 113° 28'$; $oP : P\infty = 159° 34'$. Cleavage sometimes distinct, parallel to ∞P; less distinct, parallel to the orthodiagonal and to $- P$. The mineral sometimes also occurs massive, rarely lamellar. Hardness = 5—5·5. Specific gravity = 3·4—3·56. Lustre adamantine to resinous. Colour brown, grey, yellow, green, and black. Streak white, slightly reddish in greenovite. Transparent to opaque. Brittle. The yellow varieties do not alter in colour before the blowpipe; the others turn yellow; they all slightly intumesce, and fuse on the edges to a black enamel. With borax they yield a clear yellowish-green glass. The mineral is imperfectly soluble in hot hydrochloric acid, and, if the solution be concentrated in contact with tin, assumes a fine violet colour.

Analyses.—*a.* From the St. Gothard (**Cordier**, J. des Mines, No. lxxiii. 67).—*b.* Felberthal in the Pingzau (**Klaproth**, *Beiträge*, i. 245; v. 239).—*c.* Schwarzenstein in the Zillerthal: yellow-green; specific gravity = 3·535 (H. **Rose**, Gilb. Ann. lxxiii. 94; Pogg. Ann. lxii. 253).—*d.* Arendal: brown (**Rosales**, see H. **Rose**).—*e.* Passau: brown (**Brooks**, see H. **Rose**).—*f.* St. Marcel, Piedmont: *Greenovite* (**Delesse**, Ann. Min. [4], vi. 825).—*g.* The same (**Marignac**, Ann. Ch. Phys. [3], xiv. 47).—*h.* Frugard, Finland: black-brown; specific gravity = 3·45 (**Arppe**, Analyser af finsk. Min. p. 34).—*i.* Grenville, Canada: brown; specific gravity = 3·49—3·51 (**Hunt**, Sill. Am. J. [2], xv. 442):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Silica	28·0	36	32·29	31·20	30·63	30·1	32·26	31·03	31·83
Titanic oxide	33·3	46	41·58	40·92	42·56	42·5	38·57	43·57	40·00
Lime	32·2	16	26·61	22·25	25·00	24·0	27·65	21·76	28·31
Ferrous oxide	. .	. .	0·96	5·06	3·93	. .	0·76	0·75	
Manganous oxide	. .	. .	. .	. .	. .	3·2	0·76		
Magnesia	. .	. .	. .	. .	. .	. .	. .	0·08	
Alumina	. .	. .	. .	. .	. .	. .	. .	1·05	
Loss by ignition	. .	. .	. .	. .	. .	. .	. .	0·38	0·40
	93·5	98	101·44	99·43	102·12	99·8	100·00	98·62	100·54

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* With trace of manganic oxide.

Most of these analyses may be nearly represented by the formula $\mathrm{Ca''O}\left\{\begin{matrix}\frac{1}{2}\ \mathrm{SiO^2}\\ \frac{1}{2}\ \mathrm{TiO^2}\end{matrix}\right. =$ $\mathrm{Ca''SiO^3.Ca''TiO^3}$, requiring 31·13 silica, 40·49 titanic oxide, and 28·38 lime. In the brown varieties of sphene the lime is partly replaced by ferrous oxide, in the mineral from Arendal to the amount of one-seventh.

The species was formerly divided into sphene and titanite, the former including the lighter-coloured, the latter the brown and black varieties. The name sphene is derived from σφὴν, a wedge, alluding to the usual form of the crystals.—*Greenovite*, from St. Marcel, was shown to be identical in crystalline form with sphene by Breithaupt (Pogg. Ann. lviii. 257) and Descloizeaux (Ann. Ch. Phys. [3], xx. 84).—*Ligurite*, from a talcose rock in the Apennines, has, according to Dufrenoy, the angles and characters of sphene.

Sphene occurs in imbedded crystals, in gneiss, granite, mica-slate, and granular limestone; also in beds of iron-ore, in syenite, as at Strontian in Argyleshire, and in volcanic rocks, as at Lake Laach, and Andernach on the Rhine. (Dana, ii. 269.)

SPHENOCLASE. A mineral occurring in parallel layers of various thickness in a bluish granular limestone at Gjellebäck in Norway. It is of a pale greyish-yellow colour, translucent on the edges, has a splintery fracture, and often breaks into wedge-shaped fragments when struck. Specific gravity = 3·2. Hardness nearly equal to that of orthoclase. Fusible. Gives by analysis:

$\mathrm{SiO^2}$.	$\mathrm{Al^2O^3}$.	$\mathrm{Fe^2O^3}$	CaO.	MgO.	MnO.
46·08	13·04	4·77	26·50	6·25	3·23

leading to the formula $\mathrm{3(4M''O.3SiO^2).(2R^2O^3.3SiO^2)}$. (Von Kobell, J. pr. Chem. xci. 344.)

SPHENOMITE. Shepard's name for a peculiar mineral resembling sphene, which he supposes to exist in certain meteorites.

SPHEROÏDAL STATE. See HEAT (iii. 88).

SPHEROSIDERITE. A variety of native ferrous carbonate, occurring in greenstone at Hanhau, Steinheim, Dransberg, and other places.

SPHEROSTILBITE. See STILBITE.

SPHERULITE. *Kidneystone.* These names are applied to certain spherical granules occurring imbedded in pitchstone and pearlstone. They are of grey, yellow, or red colour, with little or no lustre, translucent or opaque, and have a splintery fracture; hardness = 7: specific gravity = 2·4 to 2·5. Analysis by Erdmann (J. techn. Chem. xv. 32), 77·20 per cent. $\mathrm{SiO^2}$, 12·47 $\mathrm{Al^2O^3}$, 2·27 $\mathrm{Fe^2O^3}$, 3·34 CaO, 0·73 MgO, 4·27 $\mathrm{Na^2O}$ and $\mathrm{K^2O}$ (= 100·28).

SPIDER. Spider-threads appear to consist essentially of the same substance as silk and gossamer-threads, viz. sericin (p. 235).—The excrements of the spider contain guanine. (Handw. d. Chem. viii. 99.)

SPIGELIA. A genus of plants belonging to the gentianaceous order. *Sp. anthelmintica*, a South American annual, contains, according to Feneulle (J. Pharm. ix. 197), in the leaves, together with fixed oil, and in the root together with volatile oil, an amorphous, very bitter, nauseous substance, soluble in water and in alcohol, to which he attributes the anthelmintic action. Ricord-Madiana (Brandes, Archiv. xxv. 28), on the other hand, did not find any such substance.

SPIKE-OIL. *Oleum spicæ.*—A volatile oil, obtained by distilling *Lavandula Spica* with water. It has a less agreeable odour than true lavender-oil, is specifically heavier, and is said to deposit a larger quantity of camphor. According to Gastell, spike-oil is obtained from the leaves and stalks, true lavender-oil from the flowers, of several species of *Lavandula*. Spike-oil is frequently adulterated with oil of turpentine, which may be detected by its smaller solubility in alcohol. According to Gastell, pure spike-oil does not require more than 5 pts. alcohol, of specific gravity 0·894, to dissolve it.

SPILANTHES OLERACEA. An annual synantherous plant, indigenous in India and in South America. It has a sharp taste, apparently due to the presence of a volatile oil. The alcoholic tincture of the leaves and flowers is known as Paraguay red.

Spilanthes tinctoria contains a substance which yields indigo on exposure to the air.

SPINACH. *Spinacia oleracea.*—The leaves of this well-known culinary herb, belonging to the chenopodiaceous order, contain, according to Braconnot, acid oxalates, malates, and phosphates. Richardson (Jahresb. 1847, p. 1074) found in the air-dried plant 2·03 per cent. ash; and Saalmüller (Ann. Ch. Pharm. lviii. 389) found in the plant, dried at 100°, 10·7 per cent. ash, containing:

K^2O.	Na^2O.	CaO.	MgO.	SO^3.	SiO^2.	P^2O^5.	$Fe'''PO^4$.	$NaCl$.	Fe^2O^3.	
9·7	35·0	13·1	5·3	9·3	3·1	7·9	8·7	7·9	. .	Richardson.
23·4	24·6	10·6	7·5	4·4	5·9	8·6	. .	12·8	2·1	Saalmüller.

SPINDLE-TREE. *Euonymus europæus.* A celastraceous tree, the light wood of which yields good charcoal for gunpowder. The red seed-capsules have a saline taste, and contain grape-sugar, cerin, tannin, resins, citric acid, &c. The orange-coloured seed-coating contains a fat oil, which dissolves out the colouring-matter when expressed.

The rose-coloured shell of the seed contains tannic acid, gum, mineral constituents, &c.; the kernels contain 3·9 per cent. resin and 28·1 fat oil, together with emulsin, sugar, &c.

SPINDLE-TREE OIL. The fatty oil expressed from the seeds of the spindle-tree is clear, viscid, red-brown, yellow in thin layers, has a repulsive odour, and a bitter taste, with irritating after-taste. Specific gravity = 0·938. It is sparingly soluble in alcohol, easily in ether. It solidifies between 12° and 16°, a considerable portion of the colouring-matter separating out with the fat, and remaining, if the oil is carefully melted, in beautiful red granules on the sides of the vessel.

The oil contains, in addition to the colouring-matter, a bitter resin called by Riederer (Buchner's Repert. [2], xliv. 1) *spindle-tree bitter* or *euonymin*; also volatile acids. By the saponification of the fat-oil, Schweizer (J. pr. Chem. liii. 437) obtained oleic and margaric, together with acetic and benzoic acids, the last two remaining in the under-ley after the saponification of the oil.

Spindle-tree oil is prepared chiefly in Switzerland, where it is used for burning in lamps, and for destroying vermin in the hair of men and animals, also as an application to wounds.

SPINEL. *Spinelle*, including *Ceylanite* or *Pleonaste*, *Spinelle Ruby*, *Balas Ruby*, *Almandine Ruby*, *Candite*, *Gahnite* or *Automolite*, *Dysluite*, *Hercinite*, *Kreittonite*, *Chlorospinel.*—A mineral species represented by the general formula $M''O.\bar{R}^2O^3$, in which M'' = Mg, Fe, Ca, Zn, and Mn; and $\bar{R}'''$ = Al or Fe. The crystalline form is monometric, generally the cube, rhombic dodecahedron, and intermediate forms, also with cubic faces (CRYSTALLOGRAPHY, *figs*. 172, 174, 175, 176, 178, 199, 200.) Cleavage octahedral. Twins like *fig*. 319 (ii. 160).

Hardness = 8. Specific gravity = 3·5—4·9. Lustre vitreous. Colour red, especially carmine-red; also bluish-red to blue, brown, or yellow; pure magnesic aluminate, $MgAl^2O^4$, is colourless. Transparent to nearly opaque. Fracture conchoïdal, brittle. Infusible before the blowpipe. Insoluble in acids, but becomes completely soluble after fusion with acid potassic sulphate. Gives with fluxes the reactions of iron, and occasionally of chromium.

The name *spinel* is restricted by Rammelsberg and others to the varieties consisting of nearly pure magnesic aluminate, and having only a small proportion of the magnesia replaced by ferrous oxide; while those in which the proportion of iron is larger are regarded as forming a distinct species, called *Ceylanite*, *Pleonaste*, *Candite*, or *Chrysomelane*: they all, however, crystallise in the same forms, and the gradations of chemical composition are not very sharply defined.

Pure magnesian spinel, $MgO.Al^2O^3$, would contain 71·97 per cent. aluminium and 28·03 magnesia. Red (precious) spinel from Ceylon contains, according to Abich's analysis (corrected by Rammelsberg), 70·43 alumina, 1·12 chromic oxide, 26·75 magnesia, and 0·73 ferrous oxide; blue spinel from Aker in Sweden contains, according to the same authority, 70·53 alumina, 26·31 magnesia, and 3·57 ferrous oxide. Precious spinel is distinguished by several names, according to its colour, the deep red variety being called *ruby spinel*, the pale red *balas ruby*, the brownish-red (from its resemblance to some garnets) *almandine ruby*, and the yellowish-red *rubicelle*.

The following are analyses of the more ferruginous varieties, ceylanite or pleonaste (*Rammelsberg's Mineralchemie*, p. 162):

A. *Containing all the iron as ferrous oxide.*—*a.* Härmala in Finland (Thoreld).—*b.* Barsowskoi, near Kyschtimsk in the Ural (Abich).—*c.* Tunaberg in Sweden: dark-green (A. Erdmann).—*d.* Ronsperg in Bohemia, *Hercinite* (Quadrat).

B. *Containing ferric as well as ferrous oxide.*—*a.* Vesuvius (Abich).—*b.* Franklin, New Jersey: large greenish-black octahedrons, accompanied by red zinc-ore and calcspar (Vogel).—*c.* Stulgrabe, near Arendal in Norway (Scheerer).—*d.* Ceylon (C. Gmelin).—*e.* Iserwiese in the Riesengebirge (Abich):

	A.				B.				
	a.	*b.*	*c.*	*d.*	*a.*	*b.*	*c.*	*d.*	*e.*
Alumina	67·90	66·95	62·95	61·17	68·31	67·01	58·12	59·00	61·30
Ferric oxide	. .	. .	. .	. .	3·37	2·47	11·41	10·54	7·09
Ferrous oxide	11·88	14·33	23·46	35·67	2·06	8·55	11·88*	11·86	13·42
Magnesia	19·00	18·03	13·03	2·92	26·26	21·97	18·59	18·60	18·19
Zinc-oxide	1·38								
	100·16	99·31	99·44	99·76	100·00	100·00	100·00	100·00	100·00

Gahnite or *Automolite*, from Fahlun in Sweden, is a spinel in which the magnesium is wholly or in great part replaced by zinc (ii. 757).

Kreittonite is a black spinel, of specific gravity 4·49, nearly allied to gahnite, and containing, according to v. Kobell, 49·62 per cent. Al^2O^3, 18·48 Fe^2O^3, 26·67 ZnO, 3·40 MgO, and 1·44 MnO (= 99·61).

Dysluite (ii. 360) from Sterling, New Jersey, is a ferrico-aluminate of zinc and manganese, containing 30·49 per cent. Al^2O^3, 41·93 Fe^2O^3, 16·80 ZnO, 7·60 MnO, 2·96 silica, and 0·40 water. (Thomson.)

Chlorospinel is a grass-green spinel from Slatoust, of specific gravity 3·591—3·594, containing, according to H. Rose:

Al^2O^3.	Fe^2O^3.	MgO.	CuO.	CaO.		
64·13	8·70	26·77	0·27	0·27	=	100·14
57·34	14·77	27·49	0·62	. .	=	100·22

Spinel occurs imbedded in granular limestone, and with calcareous spar in serpentine and gneiss; it also occupies the cavities of volcanic rocks. In Ceylon, Siam, and other Eastern countries, it occurs of beautiful colours, as rolled pebbles in the channels of rivers.

SPINELLANE. A blue variety of nosean (iv. 135).

SPINTHENE. Syn. with SPHENE (p. 398).

SPIRÆA ULMARIA. *Meadow-sweet.*—The flowers of this rosaceous plant yield by distillation with water, a volatile oil consisting for the most part of salicylol (p. 167), which however appears not to exist ready-formed in the plant, but to be produced by the action of water; it contains also a neutral oil (likewise obtained by agitating the distilled water with ether), composed of 71·2 per cent. carbon, 10·1 hydrogen, and 18·7 oxygen, and a camphoroïdal substance, which crystallises in white nacreous scales, and remains solid at ordinary temperatures.

When the dried flowers of meadow-sweet are exhausted with ether, a colouring-matter called spiræin is dissolved out, together with fat, wax, traces of a neutral volatile oil, and a volatile acid, but no salicylol. The volatile oil is the same that is obtained, together with salicylol, by distilling the flowers with water. The volatile acid just mentioned is found also in the watery distillate; it crystallises in colourless needles, dissolves easily in water, with difficulty in ether, and colours ferric salts red. (Handw. d. Chem. viii. 100.)

SPIRÆIN. (Löwig and Weidmann, J. pr. Chem. xix. 236.)—The yellow colouring-matter of the flowers of *Spiræa ulmaria*, whence it may be extracted by ether. The ethereal solution is precipitated by water, the precipitate is dissolved in hot alcohol, which on cooling deposits a quantity of fatty matter; the filtered liquid is evaporated; and the spiræin thereby deposited is dissolved several times in alcohol.

Spiræin thus obtained is a yellow crystalline powder, insoluble in water, very soluble in ether and in alcohol; the solutions are of a deep green colour when concentrated, yellow when dilute, and redden litmus slightly. Spiræin is not volatile without decomposition. It gave by analysis 59·62—59·94 per cent. carbon and 5·32—5·14 hydrogen, whence Löwig and Weidmann deduce the formula $C^{30}H^{30}O^{14}$, requiring 58·6 C, 4·9 H, and 36·5 O. Gerhardt suggested $C^{21}H^{24}O^{10}$, which however does not agree so well with the analysis.

Hot concentrated *nitric acid* dissolves spiræin, forming a red solution, and decomposes it only after prolonged boiling, but without formation of oxalic acid. It dissolves without alteration in *sulphuric acid*, and is precipitated therefrom by water. Hydrochloric acid has no action upon it.—With *bromine* it forms a red mass, consisting of several substitution-products.—When oxidised by *chromic acid*, it yields formic and carbonic acids.—It dissolves with yellow colour in caustic *alkalis*, decomposes *potassic carbonate* when heated, and is precipitated from its alkaline solutions by acids. The same solutions turn brown and decompose on exposure to the air.

The alcoholic solution of spiræin forms yellow precipitates with *baryta-water*, *sulphate of aluminium*, and *tartar-emetic*; with *acetate of lead* a crimson precipitate, which blackens on drying; with *ferrous salts* a dark-green, with *ferric salts* a black precipitate; with *zinc-salts* mixed with a little ammonia, a yellow precipitate soluble in excess of ammonia; with *cupric salts* a grass-green precipitate; with *nitrate of silver* on addition of ammonia, a black precipitate insoluble in ammonia; with *mercurous nitrate* a yellowish-brown precipitate which soon becomes dark-brown; no precipitate with mercuric or platinic chloride.

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* With manganous oxide.

SPIRIT. *Spiritus.*—The word spirit was used in old chemical language as a generic name for liquids obtained by distillation. At the present day it is applied in ordinary language chiefly to ethylic alcohol, which is called *spirit of wine*, and methylic alcohol, which is also called *wood-spirit*. In pharmaceutical language it is still used as a generic name for aromatic alcoholic distillates and certain alcoholic solutions—e.g., *Spiritus cochleariæ, Sp. lavandulæ, Sp. camphoratus, Sp. saponatus.*

Spiritus abstractus, Sp. aromaticus.—These names, especially the latter, are applied to odoriferous products obtained by distilling various substances with moderately strong aqueous alcohol; they are further distinguished as *Spiritus aromaticus simplex*, and *compositus.*

Spiritus aceti dulcificatus, s. *Sp. dulcis* } or *Liquor anodinus vegetabilis.* A solution
Spiritus acetico-æthereus } of acetic ether in alcohol.

Spiritus Aeruginis, s. *Sp. Veneris, Spirit of Verdigris.*—An old name of the concentrated acetic acid obtained by distilling crystallised cupric acetate (i. 10).

Spiritus aromaticus, s. *Sp. abstractus.*

Spiritus Ceræ, Spirit of Wax.—The watery liquid containing empyreumatic oils, acetic acid, &c., obtained by the dry distillation of wax.

Spiritus Cornu Cervi, Spirit of Hartshorn.—The solution of impure ammonium-carbonate obtained by the distillation of animal matters (i. 190).

Spiritus Mindereri.—An aqueous solution of ammonium-acetate (i. 13).

Spiritus muriatico-æthereus, s. *Spiritus Salis dulcis, Sweet Spirit of Salt, Heavy Hydrochloric Ether.*—The product obtained by saturating alcohol with hydrochloric acid and distilling it over peroxide of manganese, or by distilling a mixture of alcohol and sulphuric acid over a mixture of common salt and peroxide of manganese (ii. 532).

Spiritus muriaticus.—Hydrochloric acid.

Spiritus nitro-acidus.—Nitric acid.

Spiritus nitro-æthereus, s. *Sp. dulcis, Sweet Spirit of Nitre.*—(See NITROUS ETHERS, iv. 76.)

Spiritus rector.—Boerhave supposed that volatile oils were compounds of resins, with a peculiar odoriferous substance which he called by this name.

Spiritus Sali ammoniacus, Salmiakgeist.—Aqueous ammonia.

Spiritus Salis dulcis.—See *Spiritus muriatico-æthereus.*

Spiritus Salis fumans, or *Sp. Salis fumans Glauberi.*—Fuming hydrochloric acid.

Spiritus sulphurico-æthereus.—Common ether containing alcohol.

Spiritus Sulphuris per campanam.—Obsolete name for aqueous sulphurous acid.

Spiritus Sulphuris, s. *Sp. sulphuratus volatile Beguini.*—A solution of various polysulphides of ammonium, strong enough to fume in the air (i. 194).

Spiritus sylvestris, Gas sylvestre.—An old name of carbonic anhydride.

Spiritus Tartari, Liquor pyrotartaricus.—An old name for the brownish empyreumatic liquid, containing empyreumatic oils, pyrotartaric acid, acetic acid, and (according to Göbel) formic acid, obtained by dry distillation of tartar.

Spiritus Veneris.—See *Spiritus Aeruginis.*

Spiritus Vini, Spirit of Wine.—Aqueous alcohol.

Spiritus Vitrioli.—Dilute sulphuric acid.

Spiritus Vitrioli coagulabilis.—An old name of potassic sulphate.

SPIROGYRA QUININA. A fresh-water alga, which contains 97·5 parts water to 2·5 dry substance, the latter containing 7·5 per cent. nitrogen and 0·8 ash. The ash yields 35·8 per cent. carbonates and sulphates of the alkali-metals and chloride of sodium, 1·5 carbonate of calcium, 9·8 carbonate of magnesium, 18·4 phosphate of calcium, 3·4 phosphate of magnesium, and 31·6 silica, with traces of ferric oxide. (Handw. d. Chem. viii. 150.)

SPIROL. A name applied to phenylic alcohol, because it may be obtained from spiroylic (salicylic) acid, in the same way as benzol from benzoic acid.

SPIROYL. Löwig's name for the radicle $C^7H^5O^2$ (more generally called *salicyl*, or *salicosyl*), which may be supposed to exist in oil of spiræa (salicylol). (See pp. 150, 167.)

SPIROYLIC ACID. Syn. with SALICYLIC ACID.

SPIROYLOUS ACID. Syn. with SALICYLOL.

SPIRYL, SPIRYLIC ACID, &c. Names given by Berzelius to Salicyl, Salicylic acid, &c.

SPLEEN. The largest of the "vascular" or "ductless glands" of the body. Besides albuminoïd matters (among them one precipitable by acetic acid, and containing much iron, possibly as phosphate), pigments, fats, and cholesterin, there have been found in the spleen, formic, acetic, butyric, lactic, succinic, and uric acids (the juice of spleen is acid), inosite, sarcine, xanthine, leucine, and tyrosine. In 100 parts of spleen are found water 74·031, organic matter 24·866, inorganic matters 1·103. The following table (from Ludwig) gives the percentage composition of the ashes of spleen, according to Oidtmann:

	Cl.	P^2O^5.	SO^3.	SiO^2.	K^2O.	Na^2O.	CaO.	MgO.	Fe^2O^3.	MnO.	CuO.	PbO.
Man	·55	27·11	2·54	·07	9·19	43·30	7·50	·39	7·27	·08	·01	
Woman	1·31	18·87	1·43	·72	17·41	35·12	7·26	1·02	16·20	·04	·40	·03
Infant	33·03	9·53	·50	·95	43·87		3·35	·20				

SPLINT-COAL. A hard kind of coal having a brown-black to deep black colour, resinous lustre, splintery cross-fracture, and uneven principal fracture: it is less easily inflammable than caking coal, but, when once set on fire, burns with a bright flame and great evolution of heat.

SPODUMENE. *Triphane. Swedish Zeolite.*—A silicate of aluminium and lithium (potassium and sodium), occurring in monoclinic prisms, isomorphous with augite, especially with diopside. Angle of inclined axes = 69° 40′; $\infty P : \infty P = 87°$; $oP : [2P\infty] = 130° 30'$. The crystals are usually large, exhibiting very perfect cleavage parallel to $\infty P \infty$; distinct also parallel to ∞P; in traces parallel to $[P\infty]$; seen in striæ on $[\infty P\infty]$. Twins occur with face of composition parallel to $\infty P\infty$. The mineral also occurs in cleavable masses.

Hardness = 6·5 to 7. Specific gravity = 3·132—3·137 (Rammelsberg). Lustre pearly, vitreous on the cross-fracture. Colour greyish-green, passing into greenish-white and greyish-white, rarely faintly reddish. Streak uncoloured. Translucent to subtranslucent. Fracture uneven. Before the blowpipe it loses its transparency and colour, intumesces, and melts to a glass globule; gives the reactions of lithia.

Analyses (Rammelsberg's *Mineralchemie*, p. 500).—1. Island of Utö, Südermanland, Sweden. Specific gravity = 3·133 (Rammelsberg).—2. Sterzing in the Tyrol: specific gravity = 3·137 (R.).—3. Sterling, Massachusetts; specific gravity = 3·182 (Brush); 3·073 (R.).—4. Norwich, Massachusetts: specific gravity = 3·18 (Brush):

	1		2		3		4	
	Hagen.	Rammelsberg.	Rammelsberg.	Hagen.	Rammelsberg.	Hagen.	Brush.	Smith. Brush.
Silica . . .	65·02	65·02	65·53	66·03	65·27	65·25	62·89	63·86
Alumina . .	26·84	29·14	29·04	26·45	27·47	27·55	28·42	27·84
Ferrous oxide .	0·86	. .	1·42	. .	. .		. .	0·64
Lime . . .	. . .	0·50	0·97	. .	0·30	. .	1·04	0·30
Magnesia . .	. . .	0·14	0·07	. .	0·10			
Lithia . . .	3·84	5·47	4·49	. .	2·90	. .	5·67	5·08
Soda . . .	2·68	0·46	0·07	. .	0·44	. .	2·51	0·66
Potash . .	. . .	0·14	0·07	. .	4·54	. .	. .	0·16
	99·24	100·87	101·66		101·02		100·53	H^2O 0·50
								99·04

The analyses by Hagen and Rammelsberg lead to the formula $3(Li^2O.SiO^2).4(Al^2O^3.3SiO^2)$, the lithia being partly replaced by potash and soda. A pure lithia-spodumene thus composed would contain 64·98 per cent. silica, 28·88 alumina, and 6·14 lithia. The North American specimens, except the last, had undergone some decomposition.

Spodumene occurs also at Lisens in the Tyrol, at Killiney Bay near Dublin, and at Peterhead in Scotland; also at Goshen and other localities in Massachusetts, at Windham in Maine, and Brookfield in Connecticut.

SPONGE. Sponges are organisms living in water, and consisting of a soft gelatinous mass, mostly supported by an internal skeleton composed of reticular anastomosing hairy fibres, in or among which are usually imbedded calcareous or sometimes silicious spiculæ. They are found adhering to rocks, chiefly in the Mediterranean, where they are collected by divers, and treated with hydrochloric acid to remove the lime. Two or three species are found in fresh water.

Sponge has, by some naturalists, been referred to the vegetable, by others to the animal kingdom; of late years, however, the evidence has appeared to be conclusive as to its animal nature.

The organic matter of sponges was formerly regarded as identical with horny tissue, till Posselt (Ann. Ch. Pharm. xlv. 192) and Crookewit (*ibid.* xlviii. 43) showed that it exhibits, in many respects, the same characters as the fibroïn of silk and of gossamer-threads. Städeler, however (*ibid.* cxi. 12), has shown that the organic matter of silk, when treated with sulphuric acid, yields leucine and tyrosine, whereas that of sponge yields leucine and glycocine, without a trace of tyrosine: he accordingly designates the organic matter of sponges as spongin, restricting the name fibroïn to that of silk and gossamer-threads. Schlossberger, on the other hand, designates the former as fibroïn, the latter as sericin. In some sponges, the fibroïn is combined with iodine, sulphur, and phosphorus.

Charred or burnt sponge, *Spongia usta*, has long been used in medicine; its action is, doubtless, to be attributed to the iodine which it contains. Herberger found in it 1·16 per cent. potassium-iodide, 0·702 potassium-bromide, and traces of cupric oxide. Preuss found 2·14 per cent. KI, and 0·76 NaBr. In preparing burnt sponge, care must be taken not to employ too high a temperature, as a loss of iodine may thereby be occasioned.

SPONGIN. Städeler's name for the organic matter of sponge. He prepares it by exhausting the sponge, cut up into small pieces, with dilute hydrochloric acid, then with weak soda-ley, washing it thoroughly, and drying.

SPRAT. *Clupea Sprattus*; Fr. *Espret*; Ital. *Sardino.*—These fishes, when pressed and dried, contain, in 100 parts, 64 parts water, 19 fat, and 1·94 nitrogen, equivalent to 12·3 per cent. albuminoïdal substance. They yield 2·1 per cent. ash, containing, according to Way (Jahresb. 1849, p. 658):

K^2O.	Na^2O.	CaO.	MgO.	Fe^2O^3.	SO^3.	SiO^2.	P^2O^5.	KCl.	NaCl.		
17·2	1·2	23·6	3·0	0·3	trace	trace	43·5	. .	11·2	=	100
21·9	. .	27·2	3·4	0·6	1·4	0·3	40·5	2·3	2·3	=	100

Sprats are caught in large quantities on the coasts of Sussex, Kent, and Essex, and are there used for the preparation of artificial manure.

SQUALUS. The liver of the Basking Shark, *Squalus maximus* (Linn.), yields about 80 per cent. of oil, which has a faint yellow colour, a density of 0·870 to 9·876, and a repulsive odour; does not solidify at a few degrees below 0°. By dry distillation it yields a yellow oil having the odour of acrolein, but no sebacic acid. It appears to contain a peculiar oleic acid. (Ronalds, Chem. Gaz. 1852, p. 420.)

STALAGMITES and **STALACTITES.** Deposits formed in caverns, chiefly in limestone rocks, by water filtering through the rock and taking up some of its substance, and subsequently dripping from the roof. The solution (of calcic carbonate, for instance), on exposure to the air, deposits the solid matter, which partly forms stalactites, depending from the roof like icicles, partly deposits called stalagmites, on the floor of the cavern.

STALAGMOMETER (*σταλαγμός*, drop; *μετρεῖν*, measure). An instrument employed by Guthrie for measuring the size of drops. A drop is defined as a more or less spherical mass of liquid matter, which has been separated from other matter by gravitation. Such a definition is necessary, because the term "drop" is frequently applied to a variety of liquid matters, having little or nothing in common, except shape, either as to origin or condition.

The substances concerned in drop-formation are—1. The substance to which the drop clings; 2. The substance of which it is formed; 3. The medium in which it is formed. If the drop be formed in a liquid medium more dense than the drop, the drop rises. If the dropping fluid be a gas, and the medium a liquid, the drop becomes a bubble. Hence there is no essential difference between the formation of a drop and that of a bubble; there is also an agreement in the laws which govern the sizes of the two.

The factors which are found experimentally to be most concerned in determining the size of a drop in the case of a liquid dropping from a solid through a gas are:

1. The rate at which the dropping takes place, or the growth-time, *gt*, of the drop.—2. The quantity and chemical nature of the solid matter which the dropping liquid holds in solution.—3. The chemical nature of the dropping liquid.—4. The size and shape of the solid at the part from which the drop falls.—5. The chemical nature of the solid from which the drop falls.—6. The temperature at which the dropping takes place.

In the case of a liquid dropping through a liquid, the additional factors are—7, the chemical nature, and 8, the density of the liquid medium.

The stalagmometer consists of two parts: the first to produce a perfectly uniform flow of the dropping liquid; the second to collect, and either measure or weigh, a given number of drops formed under various conditions. For particulars of the experiments and description of the different forms of stalagmometer, see Proc. Roy. Soc. (xiii. 444, 457; xiv. 22).

The following are the main laws which have been deduced:

A. *When, from a solid, a liquid drops through a gas.*

1. The drop-size depends upon the rate of dropping. Generally, the quicker the succession of the drops, the greater is the drop. The slower the rate, the more strictly is this the case. *Example:*

$$\frac{\text{Drop-size of cocoanut-oil, } gt = 0\cdot5''}{\text{Drop-size of cocoanut-oil, } gt = 12\cdot0''} = \frac{80\cdot17}{52\cdot00}$$

2. The drop-size depends upon the nature and quantity of the solid which the dropping liquid holds in solution. If the liquid stands in no direct chemical relation to the solid, the drop-size, in general, diminishes as the quantity of solid contained in the liquid increases.

3. The drop-size depends upon the chemical nature of the dropping liquid, and little or not at all upon its density; or, rather, increase of density implies increase of cohesion. Of all the liquids examined, water has the greatest and acetic hydrate the smallest drops. Water = 148·2. Glycerin = 102·8. Butyric acid = 58·0. Mercury = 57·9. Benzene = 55·2. Oil of turpentine = 50·1. Alcohol = 49·6. Acetic ether = 46·4. Acetic hydrate = 43·0.

4. The drop-size depends upon the geometric relation between the solid and liquid. If the solid be spherical, the largest drops fall from the largest spheres. The drops are largest which fall from a plane. Absolute difference in radius takes a greater effect upon the drops formed from smaller than upon those formed from larger spheres. Of circular horizontal planes, within certain limits towards the minimum size, the drop-size varies directly with the size of the plane. *Examples:*

Drop-size of water from sphere of radius		∞	=	26·5
„	„	113·1	=	24·8
„	„	47·2	=	22·6
„	„	10·0	=	14·3
„	„	7·1	=	12·8
Drop-size of water from disc of radius		5	=	16·3
„	„	4	=	14·9
„	„	3	=	9·6
„	„	2	=	7·3
„	„	1	=	4·1

5. The drop-size depends upon the chemical nature of the solid from which the drop falls, and little or not at all upon its density. Of all the solids examined, antimony delivers the least and tin the largest drops. *Example:*

Drop-size of water from		antimony	=	119·8
„	„	sulphur	=	120·2
„	„	cadmium	=	121·8
„	„	zinc	=	122·4
„	„	lead	=	122·6
„	„	phosphorus	=	122 7
„	„	bismuth	=	122·8
„	„	tin	=	124·2

6. The drop-size depends upon temperature. Generally, the higher the temperature the smaller the drop. *Example:*

Drop-size of water at		20·4° C.	=	132·6
„	„	30·6° C.	=	130·6
„	„	40 3° C.	=	129·8

B. *When, from a solid, a liquid drops through a liquid.*

7. The drop-size does not depend mainly upon the density of the medium, and consequent variation of the weight, in the medium, of the dropping liquid.

8. If there be two liquids, A and B, which drop under like conditions through air, and the drop-size of the one, A, be greater than that of the other, B, then, if a third liquid, C, be made to drop through A and through B, its drop-size through A will be greater than its drop-size through B.

9. If the drop-size of A through B be greater than the drop-size of A through C, then the drop-size of D through B will also be greater than the drop-size of D through C.

10. If a liquid, A, drop under like conditions in succession through two liquids, B and C, then its drop-size through any mixture of B and C is intermediate between its drop-size through B and its drop-size through C; and the greater the proportion of $\frac{B}{C}$ in the mixture, the more nearly does the drop-size of A through the mixture approach to the drop-size of A through $\frac{B}{C}$ alone.

11. The drop-size of any mixture of two liquids, A and B, dropping through a third liquid, C, is intermediate between the drop-size of A through C and that of B through C; and the greater the proportion of $\genfrac{}{}{0pt}{}{A}{B}$ in the mixture, the more nearly does the drop-size of the mixture approach to the drop-size of $\genfrac{}{}{0pt}{}{A}{B}$ alone, whether the dropping liquid be heavier or lighter than the liquid medium.

12. If the liquid X has a larger drop-size than the liquid Y in the liquid Z, then the liquid Z has a larger drop-size in X than it has in Y.

13. If a liquid X has a larger drop-size in air than a liquid Y, then the drop-size of X through Y is larger than the drop-size of Y through X.

14. If the drop-size of X be greater than the drop-size of Y in air, and the drop-size of Y greater than the drop-size of Z in air, then the ratio between the drop-sizes of X in any mixture of Y and Z, and the drop-size of that mixture of Y and Z through X, is greatest when the ratio between Y and Z is unity.

Laws 10 and 11 may be applied to quantitative analysis. Thus, a mixture of benzene and oil of turpentine causes water to assume a greater or less drop-size, according to the proportion of its constituents. It is easy by means of the stalagmometer to detect a difference of one per cent. in the proportion of either of the constituents.

The term "bubble" is also in common speech applied to a variety of dissimilar things. The definition adopted has been already given in speaking of drops.

In measuring the size of a drop, the barometric pressure is found to have little or no influence. In the case of bubbles it forms an important factor. Also the temperature is of greater influence with bubbles than with drops. The chief points of interest with regard to bubble-size are the influences of change in the chemical nature of the gas and of the liquid medium.

The chief results at present obtained with regard to bubble-size are these:—

15. Every different liquid causes the same gas which bubbles through it under the like conditions to assume a different bubble-size.

16. If the bubble-size of a gas through a liquid, A, be greater than its bubble-size through B, then its bubble-size through any mixture of A and B is intermediate between its bubble-size through A and its bubble-size through B.

This law is quite analogous to Law 10. Further, the singular connection between drops and bubbles is shown in the following law:—

17. If the liquid A has a larger drop-size than the liquid B in dropping through the gas C, then the gas C, in bubbling through the liquid A, has a larger bubble-size than in bubbling through the liquid B. F. G.

STANNAMYL. See Tin-radicles, Organic.

STANNATES. Salts of stannic acid. (See Tin, Oxides of.)

STANNETHYL. See Tin-radicles, Organic.

STANNIC ACID, STANNIC OXIDE. See Tin, Oxides of.

STANNIN. Syn. with Tin-Pyrites (*q.v.*).

STANNITES. Salts of stannous oxide (see Tin, Oxides of.)

STANN-METHYL. See Tin-radicles, Organic.

STANNOUS ACID, STANNOUS OXIDE. See Tin, Oxides of.

STANNUM. Syn. with Tin.

STANZAITE. Syn. with Andalusite (i. 291).

STAPELIA. A genus of apocynaceous plants, indigenous at the Cape of Good Hope. *Stapelia hirsuta*, after being scratched with a knife, yields a limpid gummy juice, which hardens to an amorphous mass on exposure to the air, and contains a bitter substance soluble in water, alcohol, and ether. (Bernap, Repert. Pharm. lxxxviii. 95.)

STAPHISAGRIC ACID. A peculiar acid, said by Hofschläger (Brandes Archiv. xix. 160) to exist in the seeds of *Delphinium Staphisagria.* It is described as white, crystalline, sublimable, and as exerting an emetic action; but the statements respecting it are very doubtful.

STAPHISAGRINE. An alkaloïd existing, according to Couerbe (Ann. Ch. Phys. [2], lii. 352), in the seeds of *Delphinium Staphisagria,* and constituting the matter insoluble in ether, obtained in the preparation of delphinine (ii. 310) from that plant. It is a slightly yellowish body, having a sharp taste, nearly insoluble in water and in ether, easily soluble in alcohol. It dissolves also in acids, but without neutralising them. It is decomposed by chlorine, and converted by hot nitric acid into a bitter resinous substance.

STAPHISAINE. Syn. with STAPHISAGRINE.

STAR-ANISE OIL. A volatile oil obtained from the seeds and seed-capsules of *Illicium anisatum*, a magnoliaceous tree indigenous in China and Japan. It has a pale-yellow colour, and resembles anise-oil from *Pimpinella Anisum* (i. 297) in taste and odour, but is more mobile, and remains liquid at + 2°. At lower temperatures it deposits a camphor or stearoptene identical with that of ordinary anise-oil. Star-anise oil likewise agrees with ordinary anise-oil in nearly all its reactions; but, according to Limpricht and Ritter, it is not directly converted by nitric acid into anisol and anisic acid, but yields an intermediate product which they designate as *anisoic acid* (i. 304).

STARCH. $C^6H^{10}O^5$ or $C^{12}H^{20}O^{10}$. *Fecula, Amidin, Amidon, Amylum, Matière amylacée. Stärke, Satzmehl, Kraftmehl.* (For a complete list of memoirs relating to Starch, down to 1862, see *Gmelin's Handbook*, xv. 72.)

This substance is very widely diffused in the vegetable kingdom, occurring in variable quantity, for a time at least, in every plant that has been examined. It is especially abundant in certain families of plants, and often occurs in very large quantity, especially in the albumen of the seed, in the cotyledons of the embryo, in the pith of stems and stalks, in bulbs, tubers, rhizomes, and roots; also in the bark and splint of trees in the winter season; sometimes in flowers.

Starch is formed in plants only when the nutriment is in excess, and is dissolved and used up at a later stage of the vegetative process, when the nutriment becomes deficient (Payen); it is probably formed from vegetable mucus (Schleiden). Before the starch appears in the cells, they are filled with a granular or a homogeneous mass, the development of which is slower than that of the cell; so that it spreads itself, in a layer of varying thickness, over the inner surface of the cell, enveloping the nucleus perhaps already present, and sometimes spreading in a thread-like form over its surface; the starch is most frequently formed in this protoplasma, more rarely on the surface or in the interior of the nucleus. (Trécul, Compt. rend. xlvii. 782.)

The following table exhibits the proportions of starch in various alimentary substances, as determined by Krocker (Ann. Ch. Pharm. lviii. 212):

Alimentary substance	Quantity of Starch in 100 pts. substance. I.	II.
Pure flour of Haricot-beans	99·96	
Wheat-flour, No. 1	65·21	66·16
„ No. 2	66·93	67·42
„ No. 3	57·70	57·21
Talavera wheat	55·92	56·29
Whittington „	53·06	51·84
Sandonier „	53·83	52·92
Rye-flour, No. 1	61·26	60·56
„ No. 2	54·84	54·12
„ No. 3	57·07	57·77
Rye (*Secale cereale*)	45·39	44·80
„ (*Sec. cer. arundin*)	47·71	47·13
Oats	27·93	36·90
„ Kamtschatka	39·55	40·17
Barley-flour	64·63	64·18
Barley	38·62	37·99
„ Jerusalem	42·66	42·03
Buckwheat-flour	65·05	
Buckwheat	43·80	44·45
Maize-flour	77·74	
Maize	65·88	66·80
Millet	55·51	53·76
Haricot-beans	37·71	37·79
Peas	38·81	38·70
Lentils	39·62	40·08
Potatoes (air-dried)	23·20	22·80
„	18·14	17·98
„	16·48	16·09

Preparation: 1. From *Wheat.*—Wheat, after being softened in cold water, is pressed under millstones or rollers, or in bags under water, as long as milky water runs off from it. This liquid, when left to itself, deposits starch containing gluten; the latter, however, dissolves for the most part in the supernatant liquid, which gradually turns sour: and on decanting this acid liquid, repeatedly stirring up the starch with fresh water, and leaving it to settle, it is at length obtained pure, and may be dried in suitable desiccating chambers. Or wheat-flour is mixed with four to five volumes of water, and $\frac{1}{8}$ to $\frac{1}{10}$ vol. sour water obtained from former operations: this sets up a fermentation, which lasts from two to four weeks, according to the temperature, and is interrupted as soon as the nitrogenised substances are decomposed and dissolved. The sediment of starch, which remains at the end of a fermentation, is repeatedly washed with water, sifted, and dried in desiccating chambers. Starch may be freed from gluten by means of cold dilute potash-ley (Kirchhoff), or distilled vinegar (Saussure); from pieces of fat and other matter, by prolonged treatment with cold water, alcohol, or ether.

2. From *Potatoes.*—Washed and rasped potatoes are drenched in a sieve with a continued stream of cold water, and the milky liquid which runs through is set aside for a few minutes, till the heavier impurities have settled down, and then left to stand for three or four hours in another pan. The starch which collects at the bottom of the clear liquid is stirred up with water, poured through hair-sieves, then left to settle, repeatedly washed with cold water, and dried, first on plates of gypsum, afterwards in desiccating chambers. The starch thus obtained is purified by successive washing with the following liquids:—1. Cold alcohol.—2. Water.—3. Water containing 0·002 per cent. hydrochloric acid.—4. Water.—5. Water containing 0·005 per cent. potash.—6. Water (Payen). After this treatment, the starch contains hydrochloric acid (Jacquelain, Gerhardt, *Traité*, ii. 486), but may be purified by boiling with alcohol containing 0·1 per cent. hydrate of potash, then washing with pure alcohol and with water.

3. From *the root-sprouts of Maranta indica and M. arundinacea:* American starch, Arrowroot.—Mode of preparation the same as from potatoes.

4. From *the roots of Janipha Manihot:* Tapioca.—The washed and bruised roots are pressed in bags under water; the starch which separates from the milky liquid is *mealy tapioca;* after drying upon hot plates, it becomes *granular tapioca;* the portion of the pulp which remains after washing and pressing is spread out on iron plates, in a layer one or two inches deep, and strongly dried into cakes; this is *Cassava-bread;* when pulverised it forms *Manjok flour*, and when again heated on iron plates till it swells up, *Mandiokka.* (Sureau, J. Pharm. xx. 622.)

5. From *the stems of several species of Sagus and Cycas:* Sago.—The starch is washed out of the pith of the stems on sieves in a stream of water, then left to settle, washed on cloths or mats, rubbed when half dry through metal sieves; and when thus granulated, it is dried at about 60° in ovens of peculiar construction.

6. From *Rice.*—Rice is heated with weak soda-ley, which dissolves the nitrogenous impurities, and leaves pure starch; then with a solution of borax, cream of tartar, or some other salts, to facilitate the separation of the starch from gluten.

7. From *Horse-chestnuts, &c.*—The same method as in 2, excepting that the starch is likewise well washed with aqueous sodic carbonate to remove the bitter principle (Flandin, Compt. rend. xxvii. 349); or merely with water, like potato-starch. (Belloc, *ibid.* xxviii. 83.)

For details on the manufacture of Starch, see Ure's *Dictionary of Arts, &c.*, iii. 745.

Properties.—Starch is a white shining powder, soft to the touch, grating between the fingers or the teeth, sometimes consisting of amorphous masses, but more frequently of granules recognisable by the microscope. These granules, of various diameter [from $\frac{1}{30}$ to $\frac{1}{800}$ of a line (Fritzsche), from ·185 to ·002 millimetre (Payen)], and various form, have commonly a small eccentric nucleus, surrounded by layers arranged concentrically one over the other. These envelopes increase by the successive deposition of new layers within the old ones, so that each layer is younger and less compactly aggregated than the one which immediately surrounds it; and since the layers are for the most part of variable thickness, they cause the granule to deviate gradually in form from the originally spherical nucleus, and assume for the most part an ovoid form. According to Maschke, the starch-granules appear like bundles of three to six concentric bladders, with light and dark rings, the light rings being formed of insoluble, the dark of soluble starch, and enclosing the central cavity of the innermost bladder, which is either empty, or filled with liquid amylone.

The following table exhibits the greatest diameter of several kinds of starch-granules, according to Payen:—

Starch from:	Millimetre.
Large Rohan potatoes	0·185
Menispermum fenestratum (colombo-root)	·180
Rhizomes of *Canna gigantea*	·175
„ „ *Canna discolor*	·150
„ „ *Maranta arundinacea* (arrowroot)	·140
Various kinds of potato	·140
Bulbs of the lily	·115
Tubers of *Oxalis crenata*	·100

Stem of a very large *Echinocactus erinaceus* (imported)	·075
Sago	·070
Broad beans	·075
Lentils	·067
Haricot-beans	·063
Peas	·050
Grain of white wheat	·050
Fresh pith of sago-tree (*Cycadeæ*)	·045
Hyacinth-bulbs	·045
Tubers of Spanish potato (*Batatas edulis*)	·045
Corms of *Orchis latifolia* and *O. bifolia*	·045
Maize (white, yellow, and violet)	·030
Fruit of Chinese sugarcane (*Sorghum saccharatum*)	·030
Stem of *Cactus peruvianus*	·030
Seeds of *Naïas major*	·030
Stem of *Cactus pereskia grandiflora*	·0225
Seeds of *Aponogeton distachyum*	·0225
Stem of *Ginkgo biloba* (*Salisburia adianthifolia*)	·022
" *Cactus brasiliensis*	·020
Fruit of *Panicum italicum*	·016
Half-grown seeds of *Naïas major*	·016
Pollen of *Globba nutans*	·015
Stem of *Cactus flagelliformis*	·015
" *Echinocactus erinaceus* (grown in hothouse)	·012
Pollen of *Rupia maritima*	·011
Stem of *Opuntia tuna* and *Ficus indica*	·010
" *Opuntia curassavica*	·010
Fruit of *Panicum miliaceum* (millet)	·010
Stem of *Cactus mammilaria discolor*	·008
Bark of *Aglanthus glandulosa*	·008
Stem of *Cactus serpentinus*	·0075
Parsneps	·0075
Pollen of *Naïas major*	·0075
Stem of *Cactus monstruosus*	·006
Seeds of beetroot	·004
" *Chenopodium Quinoa*	·002

The specific gravity of starch is 1·505 at 19·7° (Payen). When pure it is neutral, and has neither taste nor smell. It may be dried completely in a vacuum at 100°, but at ordinary temperatures it always retains a certain quantity of water (from 12 to 18 per cent.) mechanically interposed between the granules.

Starch heated to 160° is converted into dextrin (ii. 318); first, however, according to Maschke, into the soluble modification of starch mentioned below.

By dry distillation it yields carbonic anhydride, gaseous hydrocarbons, water, acetic acid, and empyreumatic oil, and leaves a porous cinder. In the open fire it softens, swells up, evolves choking vapours, and at last burns with a bright flame.

It is oxidised slowly by *oxygen*, more quickly by *ozonised air*, yielding but little carbonic anhydride. By distillation with *manganic peroxide* and *dilute sulphuric acid*, it yields carbonic anhydride, aqueous formic acid, and furfurol.

Starch, so long as it retains its natural state of aggregation, is insoluble in *water*, *alcohol*, and *ether*; but when it is placed in contact with *hot water*, the water penetrates between the different layers of which the granules are composed, swelling them up, and forming a gelatinous mass known as starch-paste, and used for stiffening linen, &c. If this paste be largely diluted with water, the swollen starch-granules slowly subside, whilst a certain quantity of amylaceous matter remains in solution.

When water into which one or two hundredths of starch has been introduced is heated to boiling, the grains swell, and disintegrate till they appear to be dissolved in the water; but on exposing the liquid to a temperature below 0°, the water freezes, and the starch, recovering a certain degree of aggregation, separates from the liquid in the form of small pellicles.

When starch is boiled under pressure at about 150°, with from 5 to 15 times its weight of water, a thin solution is obtained, which may be filtered from the insoluble portion; this liquid, as it cools, deposits minute spherical granules, which, when dried, have the whiteness of starch without its glistening aspect. These granules are slightly soluble in cold water, but are readily dissolved when the water is heated to 70° or upwards. This soluble starch, which is distinguished from dextrin (ii. 312) by being turned blue by iodine, and by possessing a greater dextro-rotatory power (=211° according to Béchamp, whereas that of dextrin is 176°), is likewise produced from common starch by the action of *diastase* at ordinary temperatures; by heating it for a certain time with *dilute sulphuric acid*; by heating with *glacial acetic acid* in a sealed tube, or with strong *nitric acid* till red vapours begin to pass off; by boiling with *chloride of zinc*; and by trituration for a short time in the cold with *strong sulphuric acid*. If, however, the action of the diastase takes place at a temperature of 65°—80° (it is completely interrupted by boiling), or if the heating with dilute acids be continued beyond a certain time, the starch is converted into dextrin, and ultimately into dextroglucose.

Starch is also converted into dextrin and sugar by boiling with aqueous *oxalic* or *dilute acetic acid*; by contact with *glutin* at a moderately high temperature, also by contact with *saliva*; into sugar also by contact with *beer-yeast*, and with various animal substances—viz., *pancreatic juice*, *gelatin*, *mucous membrane*, *urine*, *bile*, *spermatic fluid*, *blood-serum*, *animal tissue*, and by watery infusions prepared at 40° from the *heart*, *brain*, *lungs*, *liver*, *kidneys*, *spleen*, and *muscles*. (Gm. xv. 92.)

On the conversion of starch into dextrin and sugar, see also Musculus (Compt. rend. liv. 194; Ann. Ch. Phys. [3], lx. 203; Jahresb. 1860, p. 502; 1861, p. 717.)

Starch dissolves in *glycerin* when heated therewith for a considerable time, and is precipitated in the soluble modification by addition of alcohol to the solution. (W. Kabsch, Zeitschr. anal. Chem. ii. 216.)

Starch triturated in the cold with *oil of vitriol*, is converted successively into soluble starch, sulphamidonic acid, dextrin, and sugar.

With *nitric acid*, starch yields various products, according to the strength of the acid, the temperature, and the duration of the action:

a. Cold concentrated nitric acid (specific gravity = 1·52) dissolves starch without evolution of gas; water added to the solution precipitates xyloïdin or nitramidin, $C^6H^9(NO^2)O^5$, as a white powder (Braconnot, Pelouze). If water is added immediately, nothing remains dissolved; but if the solution is allowed to stand, it gives with water less and less xyloïdin, and at last none, while a substance resembling saccharic acid remains in solution. (Pelouze, Compt. rend. vii. 713.)

b. If starch is mixed with its own weight of concentrated nitric acid, and twice its weight of ordinary nitric acid ($2NHO^3.3H^2O$), and allowed to stand for 24 or 30 hours at the mean temperature, or if it is mixed with enough common nitric acid to form a thick mud, and heated in the water-bath until red fumes are evolved, unorganised insoluble starch is at first produced, then starch soluble in hot water, and lastly starch soluble in cold water (Béchamp).—Starch that has been moistened with $\frac{2}{10}$ per cent. nitric acid and water, and then allowed to dry spontaneously, yields dextrin when heated (Payen). A mixture of starch with 2 per cent. nitric acid and 4 per cent. water, dried at first in the air, afterwards in a water-bath, gives, with 5 parts of warm water, a solution which solidifies to a jelly like lichenin on cooling, and gives sugar when boiled with acids. (Mitscherlich, Pogg. Ann. lv. 121.)

c. Hot nitric acid, either concentrated or dilute, employed in excess, evolves nitrous gas and forms oxalic acid, together with malic and acetic acids.—*Nitric peroxide* acting on starch neither evolves gas nor produces oxalic acid. (Bouijs-Ballot, J. pr. Chem. xxxi. 211.)

A mixture of strong *nitric* and *sulphuric acids* converts starch into an explosive compound, analogous to or identical with gun-cotton (De Vrij, Compt. rend. xii. 126). According to Béchamp (Ann. Ch. Phys. [3], lxiv. 322), the product consists of nitroxyloïdin or dinitramidin, $C^6H^8(NO^2)^2O^5$.

Chlorine-gas, either dry or moist, does not act upon starch either at ordinary temperatures or at 100°; when starch is exposed under water to the action of chlorine for eight hours, only $\frac{1}{30}$ is decomposed, with evolution of carbonic anhydride (Liebig).—Starch distilled with *hydrochloric acid* and *manganic peroxide* yields, among other products, trichlorinated acetic aldehyde (chloral) and pentachlorinated propionic aldehyde.

When *bromine-water* is added to a solution of starch in dilute hydrochloric acid, an orange-yellow powder is formed, consisting of a compound of starch with bromine, which, however, cannot be dried without loss of bromine.

Starch-paste is coloured deep-blue by an aqueous solution of *iodine*, or by mixing it with solution of potassic iodide, and then adding a drop of chlorine-water, nitrous acid, sulphuric acid, &c., to set the iodine free. This blue coloration, which affords an extremely delicate test either for starch or for iodine, is due to the formation of a loose combination of starch and iodine, or perhaps to the mere mechanical precipitation of the iodine upon the starch, inasmuch as it is destroyed by alcohol, potash, sulphydric acid, and in general by all liquids which take up the iodine. The liquid may also be decolorised by ebullition, whereby the iodine is volatilised; if, however, the boiling be not continued for a sufficient time to volatilise the whole of the iodine, the blue colour reappears as the liquid cools. When potato-starch is powdered in a mortar with cold water, the filtered liquid is coloured blue by iodine; this effect is not observed with wheat-starch, the grains of which, being smaller, are not crushed under the pestle (Redwood, Repert. Pharm. [3], xxxix. 84). Respecting the various circumstances which affect and modify the blue colour, see *Gmelin's Handbook*, xv. 97.

Starch slowly absorbs *fluoride of boron*, becoming liquid, but without coloration.

Starch heated with five times its weight of *potassic hydrate* and a little water, gives off hydrogen at a temperature much below redness, and forms potassic oxalate (Gay-Lussac). By digestion with potash-ley for twelve hours, at 50° or 60°, it is converted into dextrin (Payen). *Soda* acts in like manner.

Starch-paste yields, with *baryta-* and *lime-water*, precipitates consisting of compounds called Amilate of barium or calcium. A dilute solution of starch, mixed with ammoniacal acetate of lead, yields a precipitate of plumbic amilate, $C^{12}H^{18}Pb''O^{10}.Pb''O$.

According to Blondeau (Compt. rend. lix. 403), starch unites with *ammonia*, forming the compound, $C^6H^{10}O^5.NH^3$ called amidia, which acts like a weak base, uniting with acids, but is not capable of decomposing metallic salts.

The aqueous solution of starch is precipitated by *tannic acid*.

Estimation and Separation of Starch.—The following method of estimating starch in vegetable organs, &c., given by Dragendorff (Jahresb. 1862, p. 631), depends upon the insolubility of starch in alcoholic potash, and its solubility in diastase and when heated with dilute acids. Two or three grains of the substance dried at 100°, and pulverised, are mixed with 25 to 30 grains of a solution of 5 to 6 pts. potassic hydrate in 94 to 96 pts. of absolute alcohol, and digested at 100° for 18 to 30 hours in a sealed tube (or a flask which can be closed airtight); and the contents are thrown, while still hot, on a weighed filter and thoroughly washed, first with hot absolute alcohol, then with cold spirit of ordinary strength, and finally with distilled water mixed (in the case of gummy substances) with a small quantity of alcohol. The filter, with its contents, is dried, first at 50°, then at 100°, and weighed. The difference between the weight thus obtained and that of the original substance gives the quantity of protein-substances, fat, sugar, and part of the salts present. The residue, together with the filter cut in pieces, is next heated with water containing 5 per cent. hydrochloric acid, till a sample is no longer turned blue by solution of iodine; and the residue separated from the acid liquid is washed, dried at 100°, and weighed. The loss of weight thus found gives very nearly the quantity of starch in the substance under examination. Any mineral substances insoluble in potash, alcohol, and water, but soluble in hydrochloric acid, that would introduce an error, may be estimated by evaporating the acid liquid to dryness, and incinerating the residue at as low a temperature as possible. This error may also be avoided by extracting the starch with concentrated extract of malt at 56°, instead of acidulated water. In the case of substances which contain a large quantity of mucus, it is best to perform the extraction with a concentrated solution of common salt slightly acidulated with hydrochloric acid, and wash the insoluble residue with weak spirit.

The residue left after the extraction of the starch contains cellulose, mucus, lignin, cuticula, and cork-substance, the last four of which may be separated from the cellulose by digestion with chlorate of potassium and dilute nitric acid.

Starch may also be estimated by converting it into glucose, and determining the quantity of that product. For this purpose Siegert (Jahresb. 1865, p. 743) digests one gramme of the air-dried substance (potatoes for instance) with 50 c.c. water and 2 grammes oil of vitriol on the water-bath for two hours; then dilutes to 100 c.c., and again warms 50 c.c. of the filtered liquid with 4 grammes of sulphuric acid to 95° for seven or eight hours. The sugar-solution thus obtained is then made up to 100 c.c. with water, or, if very much coloured, with basic acetate of lead, and the amount of sugar is determined with an alkaline cupric solution in the usual way (ii. 865).

Starch immersed in a saturated solution of *bromide* or *iodide of potassium* swells up to a pasty mass of 20 to 30 times its original volume, which dissolves in water, leaving only a very small quantity of membrane; and on adding iodine-water to the solution, the blue compound of starch and iodine is precipitated in flocks. As cellulose is not affected by bromide or iodide of potassium, these salts may be employed for detecting and separating starch in vegetable tissues. Dilute solutions act less strongly.

Animal Starch (?)—A substance, supposed to be starch, has been observed in certain parts of the animal body. Granules, which after being moistened with oil of vitriol turn blue on addition of iodine, occur in the brain, and formations of similar character occur in the spleen, liver, kidneys, and mucous membranes in certain states of disease, and in small quantity even in health. This substance, however, is not true starch, as it contains nitrogen, and does not yield sugar when heated with dilute acids.

Glycogen, the sugar-forming substance of the liver, has the same composition as starch (ii. 906).

STARS, SPECTRA OF. See SPECTRAL ANALYSIS (p. 394).

STASSFURTHITE. A borato-chloride of magnesium, occurring in the salt-beds of Stassfurth near Magdeburg, in masses having a microcrystalline structure: hardness = 4 to 5, and specific gravity = 2·913. Contains, according to the mean of recent analyses by Heintz and Ludwig, 8·20 per cent. chlorine, 2·77 magnesium, 26·24 magnesia, 60·82 boric anhydride, and 1·97 water, agreeing nearly with the formula $Mg''Cl^2.2(3Mg''O.4B^2O^3) + 4\,aq.$ (*Rammelsberg's Mineralchemie*, p. 256.)

STATICE. A genus of plumbaginaceous plants, growing in the neighbourhood of the sea or of salt-springs, and containing considerable quantities of common salt. 100 pts. of *Statice Gmelini*, air-dried, yield 7·7 per cent. ash, of which 11·5 per cent. are soluble in water, and 88·5 per cent. insoluble. *St. suffruticosa* yields 5·7 per cent. ash, of which 45·75 per cent. is soluble in water. The soluble portions of the two contain, in 100 pts.:

	K^2SO^4.	Na^2SO^4.	$NaCl$.	Na^2CO^3.	$NaHO$.
Statice Gmelini .	22·2	29·7	29·0	7·0	
Statice suffruticosa	18·4	24·8	46·0	2·7	·2

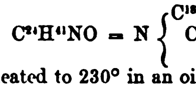
STAUROLITE. *Staurotide, Granatite, Croisette, Pierre de Croix, Schorl cruciforme grénatite.*—These names are applied to certain silicates of aluminium occurring in trimetric crystals, often forming cruciform groups, on the St. Gothard, in the Ural, and other localities. Staurolite from the St. Gothard has the composition $4Al^2O^3.3SiO^2$; that from Airolo, in Tessin, is $10Al^2O^3.9SiO^2$; that from Polewskoi, in the Ural, is $8Al^2O^3.9SiO^2$; that from Bretagne is $5Al^2O^3.6SiO^2$. (See SILICATES, p. 255; also Dana, ii. 261; Rammelsberg, p. 567.)

The name *staurolite* is also used as a synonym of harmotome.

STAUROSCOPE. An optical instrument, invented by F. v. Kobell, for examining the polarising structure of crystalline bodies. (Pogg. Ann. xcv. 320; J. pr. Chem. lxiv. 389.)

STAUROTIDE. Syn. with STAUROLITE.

STEARAMIDE. $C^{18}H^{37}NO = N\left\{\begin{matrix}C^{18}H^{35}O\\H^2\end{matrix}\right.$.—Obtained by heating ethylic stearate with alcoholic ammonia for 20 to 25 days in a sealed tube immersed in a salt-bath, and purified by recrystallisation from hot alcohol and repeated washing with cold ether. After melting it solidifies at 107·5°. (Carlet, Bull. Soc. Chim. [1859], i. 76.)



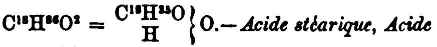
STEARANILIDE. *Phenyl-stearamide.* $C^{24}H^{41}NO = N\left\{\begin{matrix}C^{18}H^{35}O\\C^6H^5\\H\end{matrix}\right.$.—When an excess of aniline is distilled over stearic acid heated to 230° in an oil-bath, the whole of the stearic acid is converted into anilide. The product is purified by repeated crystallisation from alcohol:

$$C^{18}H^{36}O^2 + C^6H^7N = C^{24}H^{41}NO + H^2O.$$

It forms white, delicate, shining needles, melting at 93·6°, and solidifying to a mass of radiated crystals.—An alcoholic solution does not precipitate nitrate of silver.

STEARENE. See STEARONE.

STEARERIN. The fat contained in the wool of Merino sheep is, according to Chevreul (J. Pharm. xxvi. 123), a mixture of a more liquid fat, elaerin, and a more solid fat, stearerin. This latter melts at 60°, and dissolves only in 100 pts. alcohol of specific gravity 0·805, whereby it may be separated from the much more soluble elaerin. When treated with strong potash-ley, it yields a salt, stearerate of potassium, which is more like a resin-salt than a true soap. The fat is probably only a mixture.



STEARIC ACID. $C^{18}H^{36}O^2 = \left.\begin{matrix}C^{18}H^{35}O\\H\end{matrix}\right\}O$.—*Acide stéarique, Acide margareux, Talgsäure.* (Chevreul, Ann. Chim. lxxxviii. 225: Ann. Ch. Phys. [2], ii. 354; xxiii. 19; *Recherches sur les corps gras.*—Braconnot, Ann. Chim. xciii. 250.—Redtenbacher, Ann. Ch. Pharm. xxxv. 46.—Bromeis, *ibid.* xxxv. 86; xxxvii. 303.—Stenhouse, *ibid.* xxxvi. 57.—Erdmann, J. pr. Chem. xxv. 497.—Francis, Ann. Ch. Pharm. xlii. 256.—Gottlieb, *ibid.* lvii. 35.—Laurent and Gerhardt, *ibid.* lxxii. 272.—Hardwick, Chem. Soc. Qu. J. ii. 232.—Crowder, Phil. Mag. [4], iv. 21.—Heintz, see references under MYRISTIC ACID, iii. 1069.—Berthelot, Ann. Ch. Phys. [3], xli. 216, 432; xlvii. 297.—Pebal, Ann. Ch. Pharm. xci. 138.—Gm. xvii. 103.)

Stearic acid was discovered by Chevreul as a constituent of the more solid fats of the animal kingdom. It is most abundant in these, especially in beef- and mutton-suet; but exists also, together with palmitic, myristic acid, &c., in the softer fats, such as the butter of cow's milk, human fat, in that of the goose, of serpents, of cantharides, and in spermaceti. It occurs also in vegetable fats, especially in cacao-fat; less abundantly in olive-oil, in the fat-oil of black mustard, in the fat of *Brindonia indica*, and many others. The stearophanic acid, prepared by Francis from the berries of *Cocculus indicus*, and the bassic acid, obtained by Hardwick from bassia-oil, have been shown by Crowder to be identical with each other, and by Heintz to be identical with the stearic acid obtained from mutton-suet. Stearic acid appears, then, to be a frequent constituent of fats, both of the animal and of the vegetable kingdoms; it rarely, however, occurs in the free state, but almost always as a glyceride, viz. in the form of tristearin (p. 422). In the fat of cocculus-grains, part of the stearic acid is in the free state.

Preparation.—Stearic acid is prepared from beef- or mutton-suet, or better from cacao-fat, by saponifying the fat with soda-ley, heating the soap-paste with water and dilute sulphuric acid, removing the separated fatty acids after cooling, washing them with water, and then dissolving them in as small a quantity as possible of hot alcohol. On cooling, the greater part of the solid acid separates out, while the oleic acid remains in solution; and may be separated by subjecting the mass, after draining, to strong pressure, redissolving the residue in a small quantity of hot alcohol, leaving it to separate by cooling, and again pressing the solid mass. From the mixture of solid fatty acids thus obtained, the stearic acid may be separated, in a comparatively pure state, by repeated crystallisation from considerable quantities of alcohol, only the portion which first separates being each time selected. But to obtain pure stearic acid, it is better to subject the alcoholic solution of stearic and palmitic acids to fractional precipitation with acetate of lead, barium, or magnesium, the stearate then separating out first.

For this purpose Heintz dissolves the impure stearic acid (4 pts.), melting at about 60°, in such a quantity of hot alcohol that nothing will separate out on cooling, even to 0°, and mixes the hot liquid with a boiling alcoholic solution of magnesic acetate (1 pt.). The magnesium-salt which separates on cooling, is pressed and boiled for some time with a large quantity of dilute hydrochloric acid, and the stearic acid thereby separated is repeatedly crystallised from alcohol, till it melts constantly between 69° and 70°.

Stearic acid is also easily prepared from stearophanin (? tristearin), the fat of cocculus-berries, by saponifying it with potash, salting out the soap, decomposing it with hydrochloric acid, and crystallising the separated fat from alcohol. The fatty acid is thus obtained in small needles, melting at 68°: probably not quite pure stearic acid.

According to Buff and Oudemanns (J. pr. Chem. lxxxix. 215), the best material for the preparation of stearic acid is shea-butter, which contains about 70 per cent. stearic and 30 per cent. oleic acid, but no other solid fatty acid.

On the large scale, impure stearic acid is prepared for the manufacture of stearin-candles by saponifying some of the harder fats, generally with lime. The resulting lime-soap, decomposed by sulphuric acid, yields a mixture of fatty acids, which are pressed first in the cold, and afterwards at a higher temperature, in order to separate the oleic acid from the less fusible palmitic and stearic acids.

Another method, applied chiefly to palm-oil, consists in decomposing the fat with superheated steam, as described under GLYCERIN (ii. 885).—A third method consists in treating the fat with sulphuric acid and distilling the product. When a hot fat is brought in contact with strong sulphuric acid, it is immediately resolved into fatty acid and glycerin, which unites with the sulphuric acid, forming glyceryl-sulphuric acid. In the original process, patented by Gwynne, Wilson, and Jones, 37 per cent. sulphuric acid of 60°. Bm. was introduced into the hot fat, and the mixture was heated for 24 hours to 90°—92°. It was soon found, however, that the quantity of sulphuric acid might be considerably diminished (5 to 9 per cent. being sufficient for many fats), provided the temperature was raised proportionately higher (to 155° when the quantity of sulphuric acid was small). (For details of the stearin-candle manufacture, see *Ure's Dictionary of Arts*, &c., iii. 754; *Chemical Technology*, vol. i. part ii. p. 432; *Handw. d. Chem.* viii. 201.)

Properties.—Pure stearic acid crystallises from alcohol in nacreous laminæ or needles; it is tasteless and inodorous, and has a distinct acid reaction (Chevreul, Heintz). At low temperatures it is heavier than water, having a specific gravity of 1·01 at 0° (Saussure); but between 9° and 10°, its specific gravity is the same as that of water. It melts at 69°—69·2° (Heintz) to a colourless oil, which on cooling solidifies to a white, scaly, crystalline mass, lamino-crystalline on the recently-fractured surfaces. The impure acid solidifies in masses of acicular or wavellitic structure. The melting-point was found by Chevreul to be 75° (solidifying-point 70°), by Duffy 68° (solidifying-point 65·8°), by Stenhouse 69°; by Redtenbacher, Kopp, and others, 70°; by Hardwick, 70·5°. Pebal found that the purest acid melted at 69·2°.

When stearic acid is melted with more fusible fatty acids, the mixture fuses, not at the medium fusing-point, but mostly at a lower temperature, often even below that of the most fusible acid in the mixture: this phenomenon is similar to that which is exhibited by many metallic alloys, as of lead with tin, or with tin and bismuth. The following tables exhibit the melting-points and modes of solidification of mixtures of stearic acid with lauric, myristic, and palmitic acids, in various proportions, as determined by Heintz:

1. *Stearic and Lauric Acids.*

A mixture of:—

Stearic acid.	Lauric acid.	Melts at	Mode of solidifying.
10	90	41·5°	Non-crystalline
20	80	38·5	Non-crystalline, warty
30	70	43·4	Small shining crystalline facets on the surface
40	60	50·8	Warty, non-crystalline
50	50	55·8	Scarcely crystalline, slightly granular
60	40	59·0	More distinctly granular; commencement of scaly crystallisation
70	30	62·0	Somewhat more distinctly granulo-scaly
80	20	64·7	Distinctly scaly-crystalline
90	10	67·0	The same

2. *Stearic and Myristic Acids.*

A mixture of:—

Stearic acid.	Myristic acid.	Melts at	Mode of solidifying.
10	90	51·7°	Non-crystalline, opaque
20	80	47·8	Indistinctly crystalline
30	70	48·2	Lamino-crystalline
40	60	50·4	Beautiful broad laminæ
50	50	54·5	Non-crystalline, opaque
60	40	59·8	Neither needles nor laminæ; commencement of scaly crystallisation.
70	30	62·8	More distinctly scaly
80	20	65·0	Still more distinctly scaly
90	10	67·1	Scaly-crystalline

3. *Stearic and Palmitic Acids.*

A mixture of:—

Stearic acid.	Palmitic acid.	Melts at	Solidifies at	Mode of solidifying.
90	10	67·2°	62·5°	Scaly-crystalline
80	20	65·3	60·3	Finely aciculo-crystalline
70	30	62·9	59·3	The same
60	40	60·3	56·5	Rough, non-crystalline
50	50	56·6	55·0	Broad, lamino-crystalline
40	60	56·3	54·5	The same
35	65	55·6	54·3	Non-crystalline, wavy, shining
32·5	67·5	55·2	54·0	The same
30	70	55·1	54·0	Non-crystalline, wavy, dull
20	80	57·5	53·8	Scarcely acicular
01	90	60·1	54·5	Beautifully acicular

4. *Stearic, Palmitic, and Myristic Acids.*—The melting-point of a mixture of 32·5 r cent. palmitic acid with 67·5 per cent. myristic acid, which is situated at 46·2°,

sinks lower when to 20 pts. of this mixture there are added from 1 to 7 pts. of stearic acid; the melting-points of the several mixtures are as follows:—

With 1 pt. stearic acid the melting-point is		45·2°
2	„ „	44·5
3	„ „	44·0
4	„ „	43·8
5	„ „	44·6
6	„ „	45·4
7	„ „	46·0
8	„ „	46·5

These mixtures solidify to non-crystalline masses. (Heintz.)

5. *Stearic and Margaric Acids.*—Mixtures of these two acids melt more easily than stearic acid, but only a few of them less easily than margaric acid. They solidify almost in the same manner as unmixed fatty acids, differing therefore in this respect from mixtures of stearic with palmitic acid. (Heintz.)

A mixture of:—

Stearic acid.	Margaric acid.	Melts at	Mode of solidifying.
10	90	59·5°	Scaly-crystalline
20	80	59·8	The same, but less distinctly
30	70	60·8	Like the last
40	60	61·2	The same
50	50	62·0	The same, but less pearly
60	40	63·1	The same
70	30	64·7	The same
80	20	66·2	The same
90	10	67·6	Scaly-crystalline

Pure stearic acid expands very strongly when heated, especially at the moment of fusion (about 11 per cent.), and contracts so much in solidifying that cast lumps appear porous. Its volume, that at 0° being taken for unity, is 1·038 at 50°, 1·054 at 60°, 1·079 at 70°, and by fusion the volume at 70° increases to 1·198.

The volume of the solid acid at different temperatures is expressed by the formula:

$$V = 1 + 0{\cdot}0013490\, t + 0{\cdot}000034007\, t^2 + 0{\cdot}0000044180\, t^3;$$

and that of the liquid acid by—

$$V = 1{\cdot}1980 + 0{\cdot}0010098, \text{or } V' = 1 + 0{\cdot}000842\delta;$$

where V is the volume of the solid acid, = 1 at 0°; V', the volume of the liquid acid, = 1 at 70°; t denotes temperatures below 70°, and δ temperatures above 70° (Kopp, Ann. Ch. Pharm. xciii. 184). The specific gravity of the fused acid = 0·854 (Saussure). It solidifies on cooling in a scaly crystalline mass, or in shining needles.

Stearic acid distils in a vacuum, and in quantities of 15 to 20 grammes, under the ordinary atmospheric pressure, for the most part without alteration. When heated to 300—330° in a sealed tube for several hours, it does not alter either its appearance or its melting-point, or give off either gas or water. (Berthelot.)

Stearic acid is insoluble in *water*, moderately soluble in *alcohol*, more readily in *ether*, *benzene*, *sulphide of carbon*, and *oils*, both *fixed* and *volatile*.

The composition of stearic acid is determined by the following analyses:

	Calculation.		Chevreul.	Redtenbacher.	Stenhouse.	Erdmann.	Hardwick.	Francis.
C^{18} . . .	216	76·06	76·30	75·51	75·75	76·50	76·13	74·73
H^{36} . . .	36	12·68	12·43	12·86	12·78	12·81	12·86	12·46
O^2 . . .	32	11·26	11·27	11·63	11·47	10·69	11·01	12·81
$C^{36}H^{36}O^4$.	284	100·00	100·00	100·00	100·00	100·00	100·00	100·00

	Crowder.	Gottlieb.	Laurent and Gerhardt. a.	Laurent and Gerhardt. b.	Heintz.	Pebal.
C . . .	75·91	76·29	75·41	75·60	75·57 to 75·88	75·84 to 76·15
H . . .	13·01	12·83	12·53	12·61	12·59 „ 12·85	12·83 „ 12·71
O . . .	11·08	10·88	12·06	11·79		
	100·00	100·00	100·00	100·00		

The formulæ $C^{70}H^{70}O^7$ (Chevreul), $C^{68}H^{68}O^7$ (Redtenbacher, Erdmann) $C^{68}H^{66}O^7$ (Stenhouse), $C^{36}H^{36}O^4$, or $C^{18}H^{36}O^2$ (Gerhardt), have been successively proposed for stearic acid. Laurent and Gerhardt gave the formula $C^{34}H^{34}O^{4}$, or $C^{17}H^{34}O^{2}$, according to which stearic acid would be isomeric with margaric acid. The above formula, first proposed by Hardwick for stearic acid separated from bassia-oil (bassic acid), then adopted by Crowder for the stearophanic acid of Francis, has been recognised by Heintz as the true formula of stearic acid.

Decompositions.—1. When 90 grms. of stearic acid are subjected to dry distillation, the greater part passes over unchanged, but a smaller portion is resolved into carbonic anhydride, water, and stearone; the distillate likewise contains acetic acid, butyric acid, a fatty acid of lower melting-point than stearic acid; also a hydrocarbon of the formula $C^{n}H^{2n}$, and ketones richer in oxygen than stearone—these, as well as the hydrocarbons, probably resulting from further decomposition of the stearone. The black-brown residue in the retort still contains stearone, but scarcely any fatty acids. (Heintz.)

2. Stearic acid mixed with platinum-black, and heated to 100° in *oxygen-gas*, forms carbonic anhydride, and at 200° is completely converted into carbonic anhydride and water (Reiset and Millon [3], Ann. Ch. Phys. viii. 285). It burns in the air like wax, and when heated to 180° in oxygen-gas it burns with a dazzling light. With ozone it behaves like palmitic acid (iv. 334).

3. Heated with *chromic acid*, sulphuric acid, and water, it yields chromic oxide, and an acid melting at 64—65°, the alcoholic solution of which first deposits unaltered stearic acid, then an acid (Redtenbacher's margaric acid) melting between 59° and 60°. (Redtenbacher.)

4. *Permanganate of potassium* converts stearic acid into stearate and carbonate of potassium. (Cloez and Guignet, Compt. rend. xlvi. 1110.)

5. *Nitric acid* forms from stearic acid small portions of volatile acids, which mix with the unaltered stearic acid, and lower its melting-point (Heintz). When stearic acid is heated with 2 or 3 pts. nitric acid, violent action takes place after half an hour, nitric acid and pungent gases being given off, and the fused acid being converted into a tenacious frothy mass, then becoming clear and mobile, and finally solidifying as it cools to a tallowy mas, which melts at 35° to 45°. According to Bromeis, this mass contains margaric acid, and if crude stearic acid has been used, an oil formed from oleic acid, and coloured blood-red by potash. After several days' treatment with nitric acid, the stearic acid disappears completely, being converted into sebacic and succinic acids (Bromeis). In later experiments, Bromeis obtained also azoleic acid (an acid isomeric with œnanthylic acid), and produced, according to Arppe,.by the action of nitric acid on oleic acid.

6. Stearic acid fused with *phosphoric anhydride* forms a yellow mass, which, when freed from the unaltered stearic acid, melts at 54—60°, and contains, on the average, 80·4 per cent. C, 12·9 H, and 6·7 O ($C^{18}H^{34}O^{2}$ = 81·2 per cent. C, 12·77 H, and 6·03 O), and is converted by hot nitric acid into a brittle waxy mass containing 77·25 per cent. C, 12·22 H, and 10·53 O. (Erdmann, J. pr. Chem. xxv. 500.)

7. Dry *chlorine gas* at 100° converts stearic into chlorostearic acid. (Hardwick.)

8. *Bromine* heated with stearic acid and water in a sealed tube, forms a dark-brown liquid, which does not alter perceptibly at 100°, but between 130° and 140° is slowly converted into a yellow oily mixture of bromo- and dibromo-stearic acids, mixed with unaltered stearic acid. Formation of bromostearic acid:

$$C^{18}H^{36}O^{2} \quad + \quad Br^{2} \quad = \quad C^{18}H^{35}BrO^{2} \quad + \quad HBr.$$

When more than 2 at. bromine is used to 1 at. stearic acid, a large quantity of dibromostearic acid is produced, but even then a part of the stearic acid remains unaltered. If the heat is raised above 140°, the mass remains brown, or charcoal separates from it. (Oudemanns, J. pr. Chem. lxxxix. 193.)

9. *Pentachloride of phosphorus* brought in contact with stearic acid at a moderate heat, forms a colourless mass, which soon becomes heated to 150°, turning brown and black. When distilled it gives off hydrochloric acid, a small quantity of water, a hydrocarbon, stearic acid, and a solid product less soluble in alcohol than stearic acid. (Chiozza, *Gerhardt's Traité*, ii. 851.)

11. Stearate of potassium, in contact with *oxychloride of phosphorus*, becomes slightly heated, and at 150° swells up to a dark jelly, perhaps forming chloride of stearyl, inasmuch as the product treated with alcohol yields stearate of ethyl. (Pebal.)

12. When stearic acid is heated with an equal weight of *sulphur*, a trace of sulphuric acid is given off, and the same products are formed as when stearic acid is heated by itself. (Anderson, Ann. Ch. Pharm. lxiii. 373.)

13. The acid heated with *oil of vitriol* to 100°, for several hours, is decomposed, with evolution of sulphurous anhydride, and carbonises at a higher temperature. (Chevreul.)

14. Stearate of *calcium*, subjected to dry distillation, gives off marsh-gas and olefiant gas (or gases having the same composition as the latter), and yields a distillate containing a large quantity of stearone, with small quantities of other ketones, while carbonate of calcium remains behind. The distillate does not contain any fatty acid (Heintz). See STEARONE.

15. Stearic acid distilled with excess of *aniline*, yields phenyl-stearamide. From its alcoholic solution mixed with aniline, however, it crystallises unaltered. (Pebal.)

16. Stearic acid, heated with *methylic*, *ethylic*, and the *homologous alcohols*, with *mannite*, *quercite*, *pinite*, and *sugars*, with *glycerin*, *orcin*, *meconin*, *erythroglucin*, and *cholesterin*, yields ethereal compounds, formed from the acid and the other body, with elimination of water. When heated for thirty-six hours with *pyrogallic acid* to 200°, it forms a crystalline compound. (Rösing, Compt. rend. xiv. 1149.)

Stearates.—Stearic acid dissolves in a cold aqueous solution of alkaline carbonate, probably from formation of acid carbonate, but does not expel the carbonic acid, and form a mono-acid salt, till heated to about 100°. On the other hand, the stearates are decomposed by most other acids, the separated stearic acid rising to the surface as an oil when the liquid is warm. The stearates have the consistence of hard soaps and plasters, and are mostly insoluble in water.

Stearate of Ammonium.—Stearic acid, either in the fused or in the solid state, absorbs ammonia-gas without elimination of water, the quantity absorbed amounting after a month, when the absorption ceases, to 6·68 pts. ammonia for every 100 pts. of acid (1 at. NH^3 = 5·9 pts.). The compound is solid, white, inodorous, has an alkaline taste, may be sublimed in a vacuum, and then gives off ammonia, but takes it up again on cooling. When heated in a vessel containing air, it gives off ammonia and water, and yields a sublimate of acid salt, mixed with empyreumatic oil. The neutral salt, when protected from the air, dissolves in hot water, especially in ammoniacal water, and the solution on cooling deposits the acid salt in nacreous laminæ (Chevreul). The solution of stearic acid in hot dilute aqueous ammonia deposits small needles on cooling. When heated for some time, it becomes turbid, and is then not clarified by further addition of ammonia. The needles dissolve in alcohol and in ether. (Crowder.)

Stearate of Barium, $C^{36}H^{70}Ba''O^4$, is obtained by precipitating the hot alcoholic solution of an alkaline stearate with a hot solution of barium-chloride, or a hot alcoholic solution of stearic acid with a hot aqueous solution of baric acetate. It is a white crystalline powder, consisting of microscopic laminæ, and having a nacreous lustre when dry. It is insoluble in water, and decomposes without melting when heated.

Stearate of Calcium, $C^{36}H^{70}Ca''O^4$, obtained by precipitating chloride of calcium with a boiling solution of potassic stearate, and washing the precipitate with boiling water, is a white, fusible, tasteless powder.

Stearate of Copper, $C^{36}H^{70}Cu''O^4$.—Light-blue, bulky, amorphous powder; melts when heated to a green liquid, easily decomposing at the same time. (Heintz.)

Stearates of Lead.—The *monoplumbic salt*, $C^{36}H^{70}Pb''O^4$, is formed by precipitating a hot alcoholic solution of the neutral sodic salt with a hot aqueous solution of plumbic nitrate, or of the acetate containing a slight excess of acetic acid; the precipitate is washed first with alcohol, then with water. When dry it forms a heavy amorphous powder, which is not wetted by water, melts at about 125° to a colourless liquid, and solidifies to an opaque amorphous mass. It is insoluble in ether.

The *diplumbic salt*, $C^{36}H^{70}Pb''O^4.Pb''O$, is prepared by boiling stearic acid in a close vessel with triplumbic acetate, and boiling the product first with water, then with alcohol. It forms a white, transparent, friable soap-liquid at 100°. (Chevreul.)

Stearate of Magnesium, $C^{36}H^{70}Mg''O^4$, is obtained by precipitating the neutral sodic salt with sulphate of magnesium, or by supersaturating a hot alcoholic solution of stearic acid with ammonia, adding a sufficient quantity of sal-ammoniac, and then an excess of dissolved sulphate of magnesium. After recrystallisation from alcohol, it forms dazzling white flocks, consisting of microscopic laminæ, which dry up to a light fusible powder. (Heintz.)

Stearates of Mercury.—The *mercuric salt*, obtained by precipitation with mercuric nitrate, is a white easily fusible powder, which softens between the fingers.—The *mercurous salt*, obtained by precipitation with mercurous nitrate, is while moist a white granular powder, but becomes grey when dry. It is insoluble in water and in cold alcohol, slightly soluble in hot alcohol, more soluble in ether, and easily fusible.

Stearates of Potassium.—*a.* The *neutral salt*, $C^{18}H^{35}KO^2$, separates on cooling from a solution of 1 pt. stearic acid and 1 pt. potassic hydrate in 10 pts. water, in white opaque granules, and may be purified by pressure, solution in 18 pts. alcohol of specific gravity 0·821, and washing the needles, which then separate, with cold alcohol (Chevreul). According to Heintz, it is most easily obtained in the pure state, by mixing a boiling alcoholic solution of the acid with a hot aqueous solution of potassic carbonate in excess, evaporating the mass to dryness, exhausting the residue with boiling absolute alcohol, and leaving the filtered solution to crystallise. It forms shining delicate needles, scales, and laminæ, which aggregate into a hard soap; it has a faint alkaline taste.

In air saturated with moisture, it takes up one-tenth of its weight of water. One pt. of the salt forms, with 10 pts. of cold water, an opaque gum, which melts at 99°, and solidifies to a pearly gum on cooling. One pt. of the salt dissolves completely in 25 pts. of boiling water, forming a liquid which is still limpid at 92°, and solidifies to a pearly mass on cooling.

The solution of 1 pt. of the salt in 100 pts. of hot water deposits on cooling a mixture of neutral and acid stearate of potassium, while one-fourth of the entire quantity of potash remains dissolved. When the solution of the salt in alcohol, or in 20 pts. of boiling water, is mixed with 1,000 pts. of boiling water, or 5,000 pts. of cold water, it deposits all the stearic acid as acid salt, whilst half the potash remains dissolved in the water. In like manner the neutral salt, when drenched with 5000 pts. of cold water, gives up half its potash, and is converted into the acid salt without forming a gum. In these cases the alkaline water contains a trace of stearic acid in solution (Chevreul). It dissolves at 10° in 231 pts. alcohol of specific gravity 0·794, in 10 pts. at 66°, the latter solution becoming turbid at 55°, and solidifying at 38°; in 6·7 pts. of boiling alcohol of specific gravity 0·794, forming a liquid which gelatinises on cooling. It dissolves in ether-alcohol, and crystallises therefrom (Crowder, Hardwick). Boiling ether withdraws from the neutral salt a certain quantity of stearic acid, leaving a compound richer in potash. (Chevreul.)

β. The *acid salt*, $C^{18}H^{35}KO^2.C^{18}H^{36}O^2$, is obtained by decomposing the neutral salt with 1,000 pts. or more of water. When pressed, dried, and dissolved in boiling alcohol, it separates on cooling in silvery scales, inodorous, and soft to the touch. It does not melt at 100°. It is not altered by cold water, but, when boiled with 1,000 pts. of water, yields a milky liquid, consisting of a solution of the neutral salt, in which a more acid salt is suspended; towards 75° this liquid becomes clearer, but again turbid at 67°; if the liquid be filtered at the boiling heat, the more acid salt remains on the filter.

100 pts. of absolute alcohol dissolve 27 pts. of acid potassic stearate at the boiling heat, but retain only 0·36 pt. of it after cooling to 24°. In consequence of the tendency of the alcohol to decompose the acid salt into the neutral salt and stearic acid, the portion which remains dissolved contains a salt richer in stearic acid than the crystallised salt. When the acid stearate is dissolved in boiling aqueous alcohol, and the solution is mixed drop by drop with infusion of blue litmus, the liquid is ultimately reddened by the excess of acid in the salt; but on adding a larger quantity of water, which precipitates a hyperacid salt, and sets free a certain quantity of alkali, the blue colour is restored.

γ. *Hyperacid salt*, $C^{18}H^{35}KO^2.3C^{18}H^{36}O^2$ (?).—Produced when the acid salt β is decomposed by boiling water. It melts in boiling water, and solidifies on cooling; swells up in cold water. When dissolved in boiling alcohol, it separates into the acid salt which is deposited, and stearic acid which remains dissolved.

Stearate of Silver, $C^{18}H^{35}AgO^2$.—Obtained by adding a solution of 20 grms. of the sodium-salt in 5 or 6 oz. of strong alcohol to a solution of 12 to 13 grms. silver-nitrate in an equal quantity of alcohol (Crowder). Amorphous white precipitate, very loose, and strongly electric when dry. Assumes a purple colour when exposed to light in the moist state; not altered by light when dry. Insoluble in water, alcohol, and ether, easily soluble in aqueous ammonia.

Stearates of Sodium.—*a*. The *neutral* salt, $C^{18}H^{35}NaO^2$, is obtained, like the potassium-salt, by treating a hot alcoholic solution of stearic acid with excess of sodic carbonate, evaporating the solution to dryness with addition of a little water, and boiling the finely-pulverised residue with absolute alcohol, which leaves the sodic carbonate undissolved. The hot-filtered alcoholic solution is then immediately mixed with $\frac{1}{8}$ of its volume of hot water, whereupon the greater part of the sodic stearate separates on cooling in the form of a jelly, while the water retains in solution the small quantity of sodic carbonate still present. The sodic stearate thus separated is then strongly pressed, and dried between 100° and 120°.

Neutral sodic stearate is very much like the potassium-salt, but harder. From a hot, concentrated, alcoholic solution it separates as a jelly, which, on standing, is converted into shining translucent laminæ. Francis obtained it (from stearophanic acid) in prismatic crystals, having a fine mother-of-pearl lustre. It is tasteless at first, but after some time produces a distinct alkaline taste. It is permanent in air; in moderately dry air, and even from air saturated with moisture, it absorbs only 7·5 per cent. water in twelve days, afterwards not any perceptible quantity. It dissolves in 10 pts. boiling water, to a thick semitransparent mass, which solidifies and becomes opaque at 62°. When covered with 600 pts. of cold water, it becomes more opaque in 14 days by taking up water, and gives up to the water a trace of soda. With 10 pts. water at 90°, it forms a thick, nearly transparent solution, which solidifies to a white mass at 62°; and this, when heated with 40 pts. more water, forms a solution which is still filtrable below 100°, and when mixed with 2,000 pts. more water, deposits the acid salt on cooling, while half the soda and a trace of stearic acid remain in solution. It is this decomposition by water which renders the soap available for washing. It dissolves at 10° in 499 pts. alcohol of specific gravity 0·821, and in 20 pts. at the boiling heat; the latter solution becomes turbid at 70°, and solidifies on cooling to a transparent jelly, which afterwards becomes opaque, and contracts, from formation of numerous shining crystals. Boiling ether withdraws from the salt a small quantity of stearic acid, together with a trace of soda, and yields a slight deposit on cooling. (Chevreul.)

β. The *acid salt*, $C^{18}H^{35}NaO^{2}.C^{18}H^{36}O^{2}$, is formed, as above mentioned, when a solution of the neutral salt in 10 to 40 pts. of hot water is mixed with 2,000 pts. or more of cold water, or when a solution of the same salt in 2,000 to 3,000 pts. of boiling water is left to cool. It then separates in nacreous laminæ. It dissolves in alcohol, forming a solution which reddens litmus; and on addition of a large quantity of water, deposits a still more acid salt, while free alkali remains in solution.

Stearate of Strontium, $C^{36}H^{70}Sr''O^{4}$, is prepared by precipitation, like the barium-salt, which it resembles in every respect.

Substitution-derivatives of Stearic Acid.

Bromostearic Acid, $C^{18}H^{35}BrO^{2}$. (Oudemanns, J. pr. Chem. lxxxix. 195.)—Obtained by heating stearic acid (7 pts.) with water and bromine (4 pts.), in a sealed tube, to 130° or 140° at most, till the brown colour of the bromine disappears, and the mixture assumes the appearance of a yellow oil, cooling to a crystalline solid. After washing away the hydrobromic acid, the contents of the tube are dissolved in 20 times their weight of warm alcohol of 80 per cent., and the unchanged stearic acid is separated by cooling to −10°. The liquid is then mixed with an equal volume of water and an excess of crystallised sodic carbonate, and evaporated to dryness over the water-bath. The tough saline mass thus obtained is boiled with 10 volumes of alcohol of 80 per cent., and filtered as hot as possible; and the crystals of sodic bromostearate, which form in the filtrate (and of which more may be obtained by evaporating the solution), are collected and purified by repeated crystallisation from alcohol. The mother-liquor contains dibromostearate of sodium.

From the sodium-salt the bromostearic acid is separated by dilute sulphuric acid, as a yellow indistinctly crystalline mass, melting at 41°, and of specific gravity 1·0653 at 20°.

It is very slowly decomposed by heating with excess of *caustic potash*. Bromostearate of silver, heated with water, forms bromide of silver and stearidic acid, $C^{18}H^{34}O^{2}$.

The acid is insoluble in *water*, but dissolves easily in alcohol and in ether. It forms with the alkalis soap-like compounds, which crystallise from alcohol.—*Bromostearate of potassium* is more soluble than the sodium-salt. The alkaline bromostearates form precipitates with most metallic salts.

Dibromostearic Acid, $C^{18}H^{34}Br^{2}O^{2}$.—Formed as above in the preparation of bromostearic acid, and obtained in the form of an uncrystallisable sodium-salt. This salt is brown, tenacious, very hygroscopic, dissolves easily in alcohol, and forms with water an opaque soapy solution. After drying at 130°, it contains 32·5 per cent. of bromine and 6·59 of soda, approximating to the formula $C^{18}H^{33}NaBr$. (Oudemanns, *loc. cit.*).

Chlorostearic Acid, $C^{18}H^{35}ClO^{2}$. *Chlorobassic acid* (Hardwick, Chem. Soc. Qu. J. ii. 232).—Formed by treating stearic acid at 100° with dry chlorine, whereupon it first becomes thicker, and is ultimately converted into a solid resin, which forms with *potash* an amorphous soap, not crystallisable from alcohol. The *barium-salt* and *lead-salt* are insoluble in water.

STEARIC ANHYDRIDE. $C^{36}H^{70}O^{3} = (C^{18}H^{35}O)^{2}O$.—Obtained in a similar manner to benzoic anhydride (i. 557), but difficult to free from stearic acid. (Chiozza, Ann. Ch. Pharm. xci. 104.)

Benzostearic Anhydride, Benzoic Stearate, or *Stearic Benzoate,* $C^{25}H^{40}O^{3} = (C^{7}H^{5}O)(C^{18}H^{35}O)O$.—Obtained by heating potassic stearate with benzoic chloride to

100°, and exhausting the product with ether. Crystallises in shining laminæ, which melt at 100°. (Chiozza.)

STEARIC ETHERS. *a. Stearic Ethers containing the Alcohol-radicles*, C^nH^{2n+1} and $(C^nH^{2n})''$. METHYLIC STEARATE, or *Methylstearic Ether*, $C^{19}H^{38}O^2 = C^{18}H^{35}(CH^3)O^2$. (Lassaigne, Ann. Ch. Pharm. xiii. 168.)—Produced by heating 2 pts. methylic alcohol with 2 pts. sulphuric acid and 1 pt. stearic acid, or by heating stearic acid with methylic alcohol in a sealed tube for a day. It is a neutral, crystalline, semitransparent mass, insoluble in water, melting at 85°? (Lassaigne); at 38°. (Hanhart, Compt. rend. xlvii. 230.)

ETHYLIC STEARATE, commonly called *Stearic Ether*, $C^{20}H^{40}O^2 = C^{18}H^{35}(C^2H^5)O^2$. (Lassaigne, *loc. cit.*—Redtenbacher, Ann. Ch. Pharm. xxxv. 51.—Stenhouse, *ibid.* xxxvi. 58.—Francis, *ibid.* xlii. 261.—Crowder, J. pr. Chem. lvii. 292.—Heintz, see Memoirs cited, iii. 1069.—Duffy, Chem. Soc. Qu. J. v. 197.—Pebal, Ann. Ch. Pharm. xci. 153.—Berthelot, *ibid.* lxxxviii. 312.—Hanhart, Compt. rend. xlvii. 230.—Berthelot and Fleurien, Ann. Ch. Phys. [3], lxvii. 79.)—This ether is produced: 1. By heating stearic acid with alcohol to 200°; small quantities are produced also by heating the materials together to 100° for 102 hours (Berthelot); or by boiling stearic acid with alcohol (Lassaigne).—2. By passing hydrochloric acid gas into an alcoholic solution of stearic acid (Redtenbacher); by heating alcoholic stearic acid with acetic acid to 100°, the whole of the stearic acid then entering into combination in 102 hours (Berthelot).—3. By the action of alcohol on the product formed by heating stearic acid with pentachloride of phosphorus (Pebal).—4. By boiling tristearin with a solution of sodium in absolute alcohol (Duffy), or by heating tristearin with small quantities of alcoholic potash. (Bouis, Compt. rend. xlv. 35.)

Properties.—Ethylic stearate is a crystalline mass, semitransparent, and resembling white wax. Melts at 33·7° (Duffy, Heintz); at 27° (Lassaigne); 30°—31° (Redtenbacher); 31° (Hanhart); 32° (Francis); 32·9° (Pebal); 33·3° (Crowder). Solidifies to a translucent mass (Duffy); to a crystalline mass, soft at first, afterwards becoming hard and brittle (Heintz). Volatilises a little at the heat of the water-bath (Crowder); boils at 224° with partial decomposition, leaving a residue of charcoal (Duffy). Tasteless; melts on the tongue, producing a sensation of cold (Crowder); has a buttery taste (Francis). Inodorous in the cold; smells faintly when heated. (Francis.)

It dissolves very easily in *alcohol* and in *ether*, and crystallises from alcohol, but not from ether. (Duffy.)

Decompositions.—1. For the decomposition by heat, see above.—2. By water at 100°, it is partially resolved in 102 hours into alcohol and stearic acid, more abundantly by a mixture of 1 vol. acetic acid and 2 to 3 vols. water, the latter reaction taking place without any formation of acetic ether (Berthelot).—3. Fuming *hydrochloric acid* at 100°, converts it in 106 hours into chloride of ethyl and stearic acid (Berthelot).—4. It is decomposed by alcoholic but not by aqueous *potash* (Duffy).—5. Anhydrous *baryta* heated with the ether to 200° in a sealed tube, decomposes it completely, and the product heated with water yields alcoholate and stearate of barium:

$$2C^{20}H^{40}O^2 + 2Ba''O = C^{36}H^{70}Ba''O^4 + C^4H^{10}Ba''O^2.$$

These are the only products; no ethylic ether is formed (Berthelot and Fleurien).—6. Heated to 100° with *glycerin*, it does not yield stearin, even in presence of hydrochloric acid. (Berthelot.)

ETHYLENIC STEARATE, $C^{38}H^{74}O^4 + \left.\begin{matrix}(C^{18}H^{35}O)^2 \\ (C^2H^4)''\end{matrix}\right\}O^2$ (Wurtz, Ann. Ch. Phys. [3], lv. 436). *Glycolic Bistearate. Glycol distéarique.*—Obtained by the action of bromide of ethylene on stearate of silver. The product is exhausted with ether, the ethereal solution treated with potassic hydrate, and the filtrate left to evaporate. It forms light shining laminæ, melting at 76°, and resembling tristearin.

AMYLIC STEARATE, $C^{23}H^{46}O^2 = C^{18}H^{35}(C^5H^{11})O$.—Obtained by heating stearic acid with amylic alcohol to 200° in a sealed tube for a day; or by passing hydrochloric acid gas into a solution of the acid in amylic alcohol, or by boiling tristearin with a solution of sodium in amylic alcohol. It is a neutral, soft, viscous, transparent mass, melting at 25·5° (Duffy); at 25° (Hanhart). It is decomposed by alcoholic but not by aqueous potash; dissolves slightly in alcohol, the solution solidifying to a jelly. The ethereal solution does not yield crystals.

OCTYLIC STEARATE, $C^{26}H^{52}O^2 = C^{18}H^{35}(C^8H^{17})O^2$.—Obtained by heating stearic acid with octylic alcohol to 200° in a sealed tube for a day. It is colourless, inodorous, tasteless, neutral, and melts at 45°. (Hanhart, *loc. cit.*)

Cetylic Stearate, $C^{34}H^{68}O^2 = C^{18}H^{35}(C^{16}H^{33})O^2$. (Berthelot, Ann. Ch. Phys. [3] lvi. 70.)—A mixture of 1 part of ethal with 4 or 5 parts of stearic acid is heated to 200° in a sealed tube, for 8 or 10 hours. The product is mixed first with a little ether, and then with slaked lime, which takes up the uncombined stearic acid; and the whole is heated to 100° for some minutes, and afterwards boiled with ether, whereby the ethal and cetylic stearate are dissolved, and remain behind on evaporating the solution. From the mixture thus obtained, the free ethal is removed by boiling five or six times with 6 to 10 pts. of alcohol, and the undissolved cetyl-compound is then allowed to crystallise from ether. It forms broad shining laminæ, resembling spermaceti, melting at 55° to 60°, and cooling to a crystalline solid. It is neutral, but decomposes partly by volatilisation, with formation of a little free acid.

β. *Stearic Ethers containing other Organic Radicles.*—Berthelot (Ann. Ch. Phys. [3] xlvii. 324; *Chimie organique*, ii. 191—219), by heating stearic acid with *glucose, mannite, dulcite, pinite,* and *quercite*, and purifying the product in the manner described under Mannite (iii. 824), has obtained the following fatty compounds resembling stearin and palmitin:

Glucic Distearate	$C^{42}H^{78}O^7 = \left.\begin{matrix}(C^6H^6)^{vi} \\ (C^{18}H^{35}O)^2 \\ H^3\end{matrix}\right\}O^5.$
Dulcitic, Mannitic, Pinitic, Quercitic Distearate .	$C^{42}H^{80}O^7 = \left.\begin{matrix}(C^6H^8)^{vi} \\ (C^{18}H^{35}O)^2 \\ H^2\end{matrix}\right\}O^5.$
Dulcitic Tetrastearate	$C^{78}H^{146}O^9 = \left.\begin{matrix}(C^6H^6)^{vi} \\ (C^{18}H^{35}O)^4\end{matrix}\right\}O^5.$
Mannitic and Pinitic Tetrastearate . . .	$C^{78}H^{152}O^{11} = \left.\begin{matrix}(C^6H^8)^{vi} \\ (C^{18}H^{35}O)^4 \\ H^4\end{matrix}\right\}O^7.$
Mannitic Hexstearate	$C^{113}H^{216}O^{11}$?

All these compounds, when heated with hydrate of barium, are resolved into stearic acid and the respective sugars. Their formulæ require confirmation.

Camphic Stearate, $C^{28}H^{52}O^2 = \left.\begin{matrix}C^{10}H^{17} \\ C^{18}H^{35}O\end{matrix}\right\}O$? *Stearate of Camphyl. Camphol stéarique. Stearinsaures Borneol.*—Obtained by heating stearic acid with borneol (i. 626) to 200° for eight or ten hours in a sealed tube; water is then eliminated, and a mass is formed, from which the uncombined stearic acid is removed by cautious and rapid treatment with ether and slaked lime, and the free borneol by heating the evaporated ethereal solution to 150° in an air-bath for half a day or longer.

It is a thick, colourless, and inodorous oil, which solidifies to a crystalline mass after some days or months; neutral when freshly prepared; volatile (without decomposition?), decomposed by alkalis into stearic acid and borneol.—Dissolves slightly in cold, and easily in boiling alcohol and in ether. (Berthelot, Ann. Ch. Phys. [3] lvi. 89.)

Glyceric Stearates. See Stearins.

Meconic or Opianylic Stearate, $C^{46}H^{78}O^6 = \left.\begin{matrix}(C^{10}H^8)^{vi} \\ (C^{18}H^{35}O)^2\end{matrix}\right\}O^4$? *Stearate of Meconin. Stearate of Opianyl. Meconine stéarique.*—Formed by heating meconin with stearic acid to 100° for several hours; boiling the product with water, which takes up uncombined meconin; and removing the excess of stearic acid with lime and ether, as in the case of cetylic stearate. It is a neutral, white, solid mass, which melts easily, and solidifies very slowly. (Berthelot, Ann. Ch. Phys. [3] lvi. 75.)

Stearate of Orcin, $C^{25}H^{42}O^3 = \left.\begin{matrix}(C^7H^7)''' \\ C^{18}H^{35}O\end{matrix}\right\}O^2$?—When orcin (iv. 211) is heated with stearic acid to 200° in a sealed tube for some hours, a mixture is obtained from which water extracts the uncombined orcin. On separating the excess of stearic acid from the residue, by means of ether and slaked lime, the stearate of orcin remains dissolved in the ether, and may be purified by evaporation and solution in sulphide of carbon.

It is a slightly coloured, tasteless, neutral wax, which, when heated, evolves an odour of orcin and stearic acid, and volatilises. Combustible. Assumes a red colour with ammonia. Heated to 100° for some days, with moist calcic hydrate, it yields calcic stearate, and a substance soluble in water and alcohol; the latter body becomes coloured with ammonia, like orcin, but does not form crystals.

Stearate of orcin is insoluble in *water*, but easily soluble in *ether* and *bisulphide of carbon.* (Berthelot, Ann. Ch. Phys. [3] lvi. 74.)

STEARIDIC ACID. $C^{18}H^{34}O^2$. (Oudemanns, J. pr. Chem. lxxxix. 193.)—An acid isomeric with oleic acid, obtained by heating bromostearate of silver with water. It is an amorphous mass, resembling the soft animal fats; has a peculiar faint odour, melts at 35°, and distils unchanged. It dissolves in alcohol more easily than elaidic acid, and does not crystallise from the solution. With the alkalis it forms soaps, the alcoholic solutions of which give precipitates with metallic salts.

STEARINS. *Glyceric Stearates. Stearates of Glyceryl.*—Stearic ethers formed from glycerin, $(C^3H^5)'''.H^3.O^3$, by the replacement of $\frac{1}{3}$, $\frac{2}{3}$, or the whole of the typic hydrogen by the monatomic radicle stearyl. They may all be produced artificially, by heating stearic acid with glycerin; tristearin is also a constituent of most of the more solid fats of the animal and vegetable organisms.

MONOSTEARIN, $C^{21}H^{42}O^4 = \left.\begin{matrix}(C^3H^5)''' \\ C^{18}H^{35}O \\ H^2\end{matrix}\right\}O^3$. (Berthelot, Ann. Ch. Phys. [3] xli. 221.)—Prepared by heating a mixture of equal parts of stearic acid and glycerin to 200° in a sealed tube for 36 hours, then leaving it to cool. On opening the tube, there is found floating on the excess of glycerin, a solid layer, containing monostearin and uncombined stearic acid. This layer is melted, mixed with a small quantity of ether, then with slaked lime, and heated to 130° for a quarter of an hour, whereby the stearic acid is made to unite with lime. The monostearin is separated by exhaustion with ether and spontaneous evaporation.

Monostearin forms very small white needles, aggregated in roundish grains, melting at 61°, and solidifying at 60° to a hard, friable, waxy mass. It is neutral in alcoholic solution; volatilises without decomposition in a vacuum. Very slightly soluble in cold ether.

Monostearin decomposes when *heated* in a tube, with formation of acrolein. When it is heated on platinum-foil, a portion evaporates, while the rest turns yellow, and *burns* with a white very luminous flame. Heated with fuming *hydrochloric acid* to 100° in a sealed tube for 110 hours, it is almost wholly resolved into glycerin and stearic acid. A trace of a neutral chlorinated liquid is formed at the same time. Monostearin is decomposed by heating for some hours to 100° with moist *protoxide of lead*, yielding nearly 25 per cent. glycerin (calc. 25·56 p. c. $C^3H^8O^3$). It is not decomposed by heating to 100° for 26 hours with alcoholic *acetic acid.*

DISTEARIN, $C^{39}H^{76}O^5 = \left.\begin{matrix}(C^3H^5)''' \\ (C^{18}H^{35}O)^2 \\ H\end{matrix}\right\}O^3$. (Berthelot, *loc. cit.*)—Obtained: 1. By heating monostearin with 3 pts. of stearic acid to 260° for three hours.—2. By heating stearic acid with an equal quantity of glycerin to 100° for 114 hours; or to 275° for seven hours.—3. By heating the stearin of natural fats with excess of glycerin to 200° for 22 hours. Separated like monostearin. It forms white microscopic laminæ, which melt at 58°, and solidify, like monostearin, at 55°. Obtained in needles by spontaneous evaporation from ether. Neutral; decomposible by moist oxide of lead at 100°.

TRISTEARIN, $C^{57}H^{110}O^6 = \left.\begin{matrix}(C^3H^5)''' \\ (C^{18}H^{35}O)^3\end{matrix}\right\}O^3$. *Stéarine* or *Substance grasse* of Chevreul. *Suif absolu* of Braconnot. *Talgfett.* (Chevreul, *Recherches sur les corps gras.*—Braconnot, Ann. Chim. xciii. 225.—A. Vogel, *ibid.* lviii. 154.—Lecanu, Ann. Ch. Pharm. xii. 25.—Liebig and Pelouze, *ibid.* xix. 264.—Redtenbacher, *ibid.* xxxv. 195.—Francis, *ibid.* xlii. 254.—Arzbächer, *ibid.* lxx. 239.—Heintz, see Memoirs already cited (iii. 1069).—Duffy, Chem. Soc. Qu. J. v. 197, 303.—Berthelot, Ann. Ch. Phys. [3] xli. 216, 432; xlvii. 297; also *Chimie organique*, ii. 52 *et. seq.*—H. Kopp, Ann. Ch. Pharm. xciii. 194.—Bouis, Compt. rend. xlv. 35; Jahresb. 1857, p. 357.—Bouis and Pimentel, Compt. rend. xliv. 1355; Jahresb. 1857, p. 356.—Gm. xvii. 118.)—This compound was first prepared, though in an impure state, by Chevreul; purer by Braconnot. Berthelot's researches have demonstrated the identity of the stearin of natural fats with tristearin. It occurs in many fats, especially in the solid tallows and lards of the animal kingdom (p. 413).—The *stearophanin* of Francis is also resolved by saponification into stearic acid and glycerin, but differs widely from tristearin in its melting-point (p. 426).

Preparation.—Monostearin is heated for three hours with 15 to 20 times its weight of stearic acid to 270° in a sealed tube, and the product is purified in the same manner as monostearin (Berthelot). Heintz (Ann. Ch. Pharm. xcii. 300) heats stearic acid with glycerin to 200° for 24 hours, in a sealed tube filled with carbonic anhydride; the tube is then opened; the glycerin decanted; the free stearic acid removed by treatment with ether and lime; and the mass of glycerides dissolved out by boiling ether. The mixture thus obtained already contains monostearin, and may be converted into tristearin, by heating to 270° for eight hours with a large excess of stearic acid; the uncombined stearic acid may then be removed as before, and the tristearin dissolved out by hot ether.

Chevreul's stearin is obtained by dissolving mutton-suet in boiling alcohol, and recrystallising the fat, which separates out, till the melting-point becomes constant. Purer than this is Braconnot's stearin, obtained by repeatedly melting mutton-suet with oil of turpentine: still purer is that of Lecanu, who melts mutton-suet in the water-bath, adds an equal quantity of ether, stirring all the while; presses the fat when cold, and recrystallises it till the melting-point rises to 62°. Above this temperature the melting-point does not appear to be raised by repeated crystallisation from small quantities of ether; but it may still be raised by repeated crystallisation from 10 to 100 times its volume of ether. After 32 crystallisations thus performed, the melting-point rises to 69·7° (Duffy); but the fat thus treated is still a mixture of tristearin and tripalmitin (Heintz), as shown by its melting-point, and by that of the acids (= 66·5°) separated from it by saponification. The melting-points of the fatty acids obtained by saponifying different varieties of stearin, are as follows:—

Chevreul's stearin,	solidifying at	44°,	yields fatty acids melting at	53°
Braconnot's	,, ,,	61°	,, ,,	62·3°
Lecanu's	,, ,,	62°	,, ,,	66°
Liebig and Pelouze's	,, ,,	60—62°	,, ,,	64—65°
Heintz's	,, ,,	62°	,, ,,	64°

From brindonia-tallow, according to Bouis and Pimentel, pure tristearin may be separated by recrystallisation, yielding by saponification an acid having the melting-point of stearic acid.

Properties.—Tristearin forms white, pearly, shining nodules, together with very fine needles (Bouis and Pimentel); small pearly laminæ, resembling spermaceti or stearic acid (Lecanu). Inodorous; tasteless; neutral. Volatile without decomposition in a vacuum (Chevreul). A non-conductor of electricity. (Rousseau, J. Pharm. ix. 587.)

The stearin of the natural fats, as well as that artificially prepared, exhibits two (or three) different melting-points, since when heated it first becomes fluid and transparent; afterwards, when further heated, again solid and opaque; and, lastly, a second time fluid (Heintz, Duffy, Kopp). It expands when heated, but on first melting undergoes a contraction of about 2¼ per cent.; near its second melting-point it again expands, and at the moment of melting increases about 5 per cent. in volume (Kopp). Tallow-stearin melts first at 51—52°, and the second time at 62°; at 58° it is quite opaque (Heintz). With purer or less pure tallow-stearin somewhat different temperatures are observed.

This phenomenon is not produced by the splitting-up of tristearin into distearin and free acid, inasmuch as alcohol of 56° takes up no stearic acid therefrom (Heintz). According to Duffy, it is to be explained by the hypothesis of three modifications of stearin. (GLYCERIDES, ii. 879.)

α. *First modification.*—Produced when stearin melting at 69·7° is heated to 73·7° or higher, and then cooled, when it solidifies only at 51·7°. It is solid below 52°, but melts at that temperature, passing into the second modification. Shining nodules of specific gravity 0·9867 at 15°, 0·9600 at 51·5° (Duffy), 0·987 at 10°. (H. Kopp.)

β. *Second modification.*—Produced by heating stearin of the first modification to 52°, or a few degrees higher, for some time, until the fused mass has again become solid. Lamellar, melting at 64·2°. Specific gravity = 1·0101 at 15°. (Duffy.)

γ. *Third modification.*—Forms the crystals of stearin which separate from ether. It is also formed when stearin is heated to 65° or 66°, after which it solidifies slowly, at 62—63°, to an opaque, friable, highly crystalline mass, and melts again only at 69·7°. Specific gravity at 15° = 1·0179; at 51·5° = 1·009; at 65·5° = 0·9931; at 68·2° = 0·9746. (Duffy.)

The specific gravity of melted stearin at 65·5° is 0·9245 (Duffy). Duffy's second modification is not obtained from pure stearin, which, however, contains the first and third modifications, even after several recrystallisations; it is, therefore, not to be regarded as pure stearin (Heintz). Tallow-stearin, melting at 60°, possesses at 50°, in the first modification, a volume = 1·031, and after passing into the second modification a volume = 1·008, the volume at 0° being = 1; its volume increases to 1·076 at the melting-point, and on melting to 1·127. (H. Kopp.)

Melted stearin solidifies on cooling to a very indistinctly crystalline mass (Heintz); to a blistered mass, which exhibits transparent and dead-white portions (Bouis and Pimentel). The temperature of melted stearin falls several degrees below the solidifying-point before the mass becomes solid, but rises again during solidification to 44° (Chevreul), 54° (Lecanu); it forms a semitransparent mass, having an even surface, the central part of which ultimately solidifies in radiated crystals. (Chevreul.)

The percentage composition of tristearin is as follows:—

		Calculated.		Chevreul.	Lecanu.	Liebig and Pelouze.
C^{57}	. . .	684	76·85	77·7	76·91	74·52 to 76·09
H^{110}	. . .	110	12·36	11·8	12·39	12·39 „ 12·32
O^6	. . .	96	10·79	10·5	10·70	
$C^{57}H^{110}O^6$		890	100·00	100·00	100·00	

		Arzbächer.	Duffy.			Heintz.		Berthelot.
			a.	*b.*	*c.*	*a.*	*b.*	
C	. . .	76·51	77·12	76·32	76·87	76·74	76·50	75·8
H	. . .	12·28	12·30	12·32	12·20	12·42	12·41	12·4
O	. . .	11·21	10·58	11·36	10·93	10·84	11·09	11·8
		100·00	100·00	100·00	100·00	100·00	100·00	100·0

Berthelot analysed artificially-prepared tristearin. The stearin of beef-suet contains, according to Arzbächer, 78·74 per cent. C; but Heintz (*b*) and Duffy (*c*) found it to have the same composition as that from mutton-suet. Duffy examined stearin melting (*a*) at 62·5° and (*b*) at 69·7°. The formula of tristearin was deduced by Berthelot from the combining proportions of glycerin with acids (ETHERS, ii. 519; GLYCERIDES, ii. 877), Duffy having previously shown that in the formation of 1 at. stearic acid from stearin 1 at. carbon is eliminated. Berthelot's formula alone explains how, in the saponification of stearin, the undermentioned amounts of glycerin and acid are produced.

Stearin is not perceptibly soluble in *alcohol* of 30° B., nor even in alcohol of 97 per cent., in the cold; it dissolves abundantly in hot alcohol, and separates in flocks on cooling (Lecanu). 100 pts. of boiling alcohol, of specific gravity 0·795, dissolve 15·04 to 16·07 pts. of Chevreul's tallow-fat from mutton-suet; 15·48 pts, of that from beef-suet; 18·25 from hog's-lard; and 36 from goose-fat. 100 pts. of boiling alcohol of specific gravity 0·805, dissolve 6·63 pts. of tallow-fat; 100 pts. of specific gravity 0·822 dissolve 1·45 of the tallow-fat of butter, which is deposited almost entirely on cooling (Chevreul). Stearin precipitated from an alcoholic solution retains alcohol even after prolonged fusion. (Saussure.)

Stearin dissolves very freely in boiling *ether*, which retains $\frac{1}{225}$th on cooling (Lecanu). It dissolves in hot *acetone* more freely than in cold, and is precipitated on cooling, or by the addition of water (Chenevix). It is easily soluble in *volatile oils*, and mixes with melted *camphor*, and with *drying* and *oil-fat*. A solution of 1 pt. of stearin in 160 pts. almond-oil deposits white flocks of stearin when mixed with 170 pts. of ether; it is therefore not rendered more soluble in ether by admixture with a fatty oil. (Lecanu.)

Decompositions.—1. Stearin yields by dry distillation the products of decomposition of stearic acid and of glycerin—viz., carbonic anhydride, gaseous and liquid hydrocarbons, acrolein, acetic acid, water, and free carbon; part of it, however, passes over unaltered. The hydrocarbons boil between 190° and 245°, and are polymeric with ethylene (Gerhardt).—2. Pure stearin does not alter by exposure to the air, and impure stearin probably turns rancid only when it contains olein or drying oil. (Chevreul.)

3. Tristearin is easily saponified by *alkalis*, *lead-oxide*, and other bases, yielding stearic acid (melting at 70°) and glycerin, 1 at. of pure tristearin yielding 3 at. stearic acid, and 1 at. glycerin:

$$\left.\begin{matrix}(C^3H^5)'''\\(C^{18}H^{35}O)^3\end{matrix}\right\}O^3 + 3H^2O = 3\left(\left.\begin{matrix}C^{18}H^{35}O\\H\end{matrix}\right\}O\right) + \left.\begin{matrix}(C^3H^5)'''\\H^3\end{matrix}\right\}O^3.$$

Pure tristearin from *Brindonia indica* yielded 95·7 per cent. stearic acid; artificial stearin yielded 95·5 per cent. stearic acid, and 10·2 glycerin dried in vacuo (Heintz): the quantities required by calculation are 95·7 stearic acid, and 10·3 glycerin; the purity of the substance and the correctness of the formula are therefore fully proved.

4. A solution of *sodium-ethylate* in absolute alcohol decomposes stearin when heated, yielding sodic and ethylic stearate, together with glycerin: in like manner, with *sodium-amylate*, it yields amylic stearate (p. 421).

5. A solution of dry *ammonia-gas* in absolute alcohol does not act on stearin, even after prolonged boiling.

6. *Bromine* and *chlorine* decompose stearin, forming substitution-products, which are softer and more soluble than stearin itself. The chlorine-compound contains 21·2 per cent. chlorine; the bromine-compound 35·9 bromine. (Lefort, J. Pharm. [3], xxv. 24.)

7. Stearin mixed with *pancreatic juice* yields an emulsion in which the whole of the stearin is resolved into stearic acid and glycerin, on standing for a day or two at a temperature of 30—40°. (Bernard; Berthelot.)

STEAROCHLORHYDRIN. $C^{21}H^{41}ClO^{3} = \left.\begin{matrix}(C^{3}H^{5})'''\\ C^{18}H^{35}O\\ H\end{matrix}\right\}\begin{matrix}Cl\\ O^{2}\end{matrix}$.—Produced by passing hydrochloric acid gas for some time into a mixture of stearic acid and glycerin heated to 100°. After being left to settle, then washed with sodic carbonate, and repeatedly dissolved in ether, it forms a solid mass melting at 28°. (Berthelot.)

STEAROGLUCOSE. *Glucic Stearate* (p. 421). $C^{42}H^{78}O^{7} = 2C^{18}H^{36}O^{2} + C^{6}H^{12}O^{6} - 3H^{2}O$.—A saccharide produced by heating stearin with certain kinds of sugar. To prepare it, a mixture of stearin and anhydrous glucose is heated to 120° for fifty or sixty hours, and the product is purified by ether and lime, like monostearin (p. 422). Cane-sugar and trehalose also yield the same compound; when trehalose is employed, the mixture may be heated to 180°. Small quantities are obtained likewise from stearin and starch at 180°, and from stearin and woody fibre at 200°.

It forms microscopic fine granules, or a white fusible mass resembling stearin. It is neutral. It assumes with oil of vitriol a reddish colour, quickly changing to violet and black. It reduces *potassio-cupric tartrate*; is decomposed by treatment with warm alcoholic *hydrochloric acid*, with formation of glucose, humus-substances, and ethylic stearate. (Berthelot, Ann. Ch. Phys. [3] lx. 95.)

STEAROCONOTE (from στέας, tallow; and κόνις, powder).—The name applied by Couerbe to a fatty substance, which he obtained, together with others, from the brain, by exhaustion with ether and then with boiling alcohol. It is described as a yellow-brown pulverulent fat, insoluble both in alcohol and ether, unless fixed oils are also present, in which case it dissolves in ether; hence it is dissolved out of the brain by ether, and on evaporating the solution to dryness, and exhausting with alcohol, cephalote (i. 822) dissolves, and stearoconote remains behind. According to Couerbe, it contains both sulphur and phosphorus. According to Frémy, however, it is not a definite substance, but a mixture of brain-albumin, oleophosphates, and cerebric acid; and according to the more recent investigations of v. Bibra and W. Müller, all the substances found in the brain by Couerbe and Frémy are chiefly mixtures of different fatty acids. The presence of sulphur and phosphorus in these fats appears very doubtful. (See Nervous Tissue, iii. 32; also Handw. d. Chem. viii. 226).

STEAROLAURETIN. The name applied by Grosourdi (J. Chim. Méd. [3] vii. 257) to a solid fat, which separates, on standing at + 10°, from the oil obtained by warm pressure from the pericarp of bay-berries (the fruit of *Laurus nobilis*). It forms warty masses, but has not been further examined.

STEAROLAURIN. Grosourdi's name for a fat deposited, on standing at + 10° to + 4°, from the oil obtained by warm pressure from the shelled seeds (cotyledons) of the fruit of *Laurus nobilis*. It forms a yellowish-white mass.

STEARONE. $C^{35}H^{70}O = C^{18}H^{35}O.C^{17}H^{35}$. (Bussy, Ann. Ch. Pharm. ix. 269.—Redtenbacher, *ibid.* xxxv. 57.—Varrentrapp, *ibid.* xxxv. 80.—Rowney, Chem. Soc. Qu. J. vi. 97.—Heintz, Pogg. Ann. xciv. 272; xcvi. 65.)—This body, the ketone of stearic acid, is produced by the dry distillation of stearic acid, or more abundantly by that of calcic or plumbic stearate. To purify it, the solid distillate is boiled with water, the finely pulverised residue is heated with ether to the boiling-point, and after cooling, collected on a filter and again treated with ether: pure stearine then remains behind. (Heintz.)

The substance described as margarone by Bussy, Redtenbacher, and Varrentrapp, and obtained by the distillation of impure stearic acid, was a mixture of stearone and palmitone; Rowney's stearone (p. 412) is doubtless also impure stearone.

Pure stearone forms delicate, pearly, microscopic laminæ very strongly electric. It is slightly soluble in boiling *alcohol*, and separates almost entirely on cooling; nearly insoluble in cold and very slightly soluble in boiling *ether*. It melts at 87·8°. (Heintz.)

Bromostearones.—Melted stearone treated with excess of bromine, gives off hydrobromic acid, and is converted into a red oily liquid, which solidifies on agitation with water, and when washed with aqueous ammonia and then with cold alcohol, and repeatedly crystallised from ether, yields dibromostearone, $C^{35}H^{68}Br^{2}O$, in laminar crystals which melt at 72°, and are moderately soluble in cold ether.

By the further action of bromine on stearone, a very fusible substance is formed probably a more highly brominated product.

STEAROPHANIC ACID. Stearic acid from cocculus-grains (p. 413).

STEAROPHANIN. The glyceride obtained from cocculus-grains. It agrees with tristearin in nearly all its properties, but was found by Francis to melt at a much lower temperature, viz. at 35° to 36°, doubtless in consequence of the admixture of fats of lower melting-point.

STEAROPTENES. The more solid constituents of essential oils. (See OILS, iv. 184.)

STEAROYL. Weltzien's name for the hydrocarbon $C^{18}H^{35}$, which may be supposed to exist in stearone, regarding it as $(C^{18}H^{35})^{2}O$.

STEARYL. $C^{18}H^{35}O$.—The radicle of stearic acid, &c.

STEATIN. Syn. with CEREBROTE (i. 830).

STEATITE. A mineralogical term used synonymously, sometimes with SOAPSTONE (p. 324), sometimes with TALC (*q.v.*).

STEATOÏD. A name applied to serpentine occurring in pseudomorphs at Snarum in Norway.

STEEL. *Acier. Stahl.*—The particular kind of metallic iron to which this name is applied possesses characters which render it to some extent intermediate between cast-iron and what is commonly known as malleable iron, while it is distinguished from both by the capability of acquiring very considerable hardness when heated and suddenly cooled, and of becoming soft again when heated and allowed to cool slowly. Steel is generally hardened by plunging it while hot into water, oil, mercury, or some other liquid. The greater the reduction of temperature, and the more rapidly it takes place, the greater is the degree of hardness produced. Steel raised to a white heat and then immersed in cold mercury, acquires a degree of hardness nearly equal to that of the hardest white cast-iron, or even of diamond. It is then also extremely brittle. By heating such hardened steel again, and allowing it to cool gradually, it becomes softer and less brittle. It is in virtue of this capability, which is one of the most distinctive characters of steel, that various degrees of hardness may be communicated to it, by regulating the temperature to which the hardened metal is heated before being allowed to cool gradually, or to which the soft metal is heated before being suddenly cooled. Steel tools and instruments are made and finished while the metal is in the soft state, and the requisite degree of hardness is given to them as above described. This operation is called *tempering* (*tremper*; *anlassen*). The degrees to which the metal requires to be heated, in order to acquire different degrees of hardness, are indicated by the colours which it assumes when heated, and which are due to the formation of an extremely thin film of oxide on the surface. They are as follows:—

Temperature.	*Colour.*	
220°C.	Faint yellow	for surgical instruments.
230	Straw-yellow	for razors, penknives, &c.
255	Brownish-yellow	for scissors, hard chisels.
265	Purple spots	for axes, knives.
277	Purple	for table-knives.
288	Pale-blue	for sword-blades, watch-springs.
293	Dark-blue	for fine saws, boring tools.
316	Blackish-blue	for hand-saws.

The distinction between steel and cast-iron or malleable iron is not by any means absolute, but consists rather in the degree to which considerable hardness, or the capability of acquiring that character, is associated with tenacity and malleability. Accordingly, there are numerous varieties of steel approximating more or less to cast-iron or to malleable iron. Together with such differences in the nature and qualities of steel, it has generally been found that there are corresponding differences in the amount of carbon the metal contains; the closer the approximation to malleable iron, the smaller is the amount of carbon in the metal, and the reverse. When the amount of carbon is less than about 0·65 per cent., the capability of being tempered is either wanting or very slight. When it amounts to 1·75 per cent., the metal is capable of being made very hard, but its tenacity is much reduced. The capability of being hardened and tempered is combined with the maximum tenacity when the carbon amounts to about 1·5 per cent. The opinion that these characters of steel are intimately connected with the amount of carbon it contains has long been entertained; but it is still uncertain in what manner these facts are related.

Among the various substances which are frequently present in metallic iron as impurities, those which appear to be most prejudicial to the quality of steel are *sulphur* and *phosphorus*.

The fact that certain iron-ores containing *manganese* are especially suitable for the production of steel, has given rise to the opinion that this metal was a necessary constituent of good steel; but it is rarely, if ever, the case that steel contains manganese, and whatever beneficial influence the presence of this metal may exercise in the manufacture of steel, would appear to be of a totally different nature.

The presence of *chromium*, *nickel*, or *rhodium* in steel is said to improve its quality, but the data on which the opinion is founded are somewhat insufficient.

The results of observations on the influence of *silver* upon steel are discordant. *Tungsten* and *titanium* have been stated to improve the quality of steel, but further experience is requisite in regard to this question.

The presence in steel of a minute amount of *nitrogen* as a necessary constituent has been alleged by **Frémy**; but **Marchand**, **Rammelsberg**, and **Boussingault** have failed to detect, by their analyses, any greater indications of nitrogen than might be fairly referred to accidental sources. **Caron** infers, from his observations, that if steel contains nitrogen, it is not as an essential constituent. Similar results have been obtained by **Stuart** and **Baker**. (Chem. Soc. J. [2], ii. 390.)

The colour of steel is greyish-white, sometimes almost pure white, and the hardened metal is somewhat whiter than the soft metal. The lustre of steel is not remarkably different from that of malleable iron. The surfaces of fracture present a very fine granular texture, very uniform, and without any of the fibre characteristic of good malleable iron. The fracture of hardened steel presents a remarkably close fine-grained texture. Steel is always harder than malleable iron, but it is never so hard as that kind of white cast-iron known as "Spiegeleisen." The tenacity of steel is greater than of either cast-iron or malleable iron, or indeed of any other metal. According to the experiments of **Musschenbroek** and **Rennie**, it is at least twice as great as that of malleable iron. It is slightly reduced by hardening, but by annealing the metal its tenacity is rendered even greater than that of the unhardened steel.

Tenacity or Tensile Strength of Steel.

Kind of steel.	Lengthwise in pounds.	Crosswise per square inch	Ultimate extension		Authority.
			length	cross.	
Shear steel bars rolled and forged	118,468	. .	0·135	. .	Napier
Puddled steel bars rolled and forged	90,000	. .	. .	. .	Fairbairn
Cast-steel bars rolled and forged	130,000	. .	. .	. .	Rennie
Puddled steel plates . . .	102,593	85,365	·028	·013	Napier
	71,532	67,686	·082	·057	
Cast-steel plates . . .	94,289	96,308	·057	·096	"
	75,594	69,082	·198	·196	

See **Kirkaldy**, Trans. Institut. Engineers in Scotland, 1858–9; and *Tensile Strength of Wrought Iron and Steel* (London, 1862); also **Fairbairn**, Brit. Assoc. Report, 1856.

The malleability of soft steel at the ordinary atmospheric temperature is even less than that of hard cast-iron. Hardened steel is very brittle, and will not bear working with the hammer. The malleability of steel is, however, considerably increased when the metal is heated.

The specific gravity of soft steel varies between 7·6224 and 7·8131 (**Karsten**). It is somewhat reduced by hardening the metal; viz. from 7·75 to 7·55 (**Rinman**), 7·79 to 7·67 (**Pearson**).

The specific heat of steel is 0·11848 (**Regnault**). Its linear expansion, when heated from 0° to 100° C., is scarcely greater than that of malleable iron, but less than that of cast-iron (**Davy**). By heating from summer heat to red heat, a steel bar lengthens about $\frac{6}{560}$, malleable iron $\frac{4}{560}$, and cast-iron $\frac{7}{560}$; by heating to whiteness, steel lengthens $\frac{10}{560}$, malleable iron $\frac{7}{560}$, and cast-iron $\frac{12}{560}$. (**Rinman**.)

When steel is heated to whiteness, it becomes soft like malleable iron, under the same condition, and is then capable of being wrought and welded not only to steel, but also to malleable iron. It welds at a lower temperature than iron does.

The melting-point of steel is between that of cast-iron and that of malleable iron, and is probably about 1800° C. The fusibility of steel is, however, influenced by the amount of carbon it contains.

Steel is less susceptible of magnetic induction than pure iron; but it far exceeds iron in the capability of becoming permanently magnetic, for which reason it is generally used for making magnets (iii. 761).

Steel is oxidised much less readily than malleable iron by exposure to the atmosphere at the ordinary temperature, especially when it is polished and clean. When gradually heated in contact with atmospheric air, it acquires, as the temperature rises, a succession of colours at the surface, from faint yellow to blackish-blue. At 360° C. all colour disappears; but if the heat be raised still further, the colours reappear in the same order, more faintly than at first. The coloration is due to an incipient oxidation, and the succession of colours is caused by the increasing thickness of the film of oxide, as in Newton's rings it is caused by the unequal thickness of a layer of air.

Hardened steel is dissolved by acids less readily than soft steel. With dilute hydrochloric or sulphuric acids, soft steel gives a larger amount of the black graphitic substance which is attracted by the magnet, than malleable iron does. By the continued action of the acid, this substance is converted into a carbonaceous mass, which burns without leaving any residue, as in the case of malleable and cast-iron. With dilute nitric acid this substance is not separated from soft steel. Concentrated hydrochloric acid dissolves soft steel completely without residue.

Manufacture of Steel.

By smelting very rich and pure iron-ores with charcoal in a bloomery, much in the same way as that described under the head of IRON (iii. 344), steel, or a kind of steely iron, may be produced direct from the ore; but this method of manufacture, though much practised formerly, and still followed to some extent at a few places, has long been superseded by others. Steel is now generally produced indirectly, either by carbonising bars of malleable iron, or by partially decarburising cast-iron. The steel produced by the former method is called *Cement Steel* (*acier de cémentation; Brennstahl*); that produced by the latter method is called *Natural Steel* (*acier de forge; Rohstahl*), when the decarburation is effected in a finery hearth or forge similar to that used in the manufacture of malleable iron (see iii. 345). But cast-iron is also converted into steel by puddling, and by the direct action of atmospheric air on the melted metal, according to the method lately introduced by Bessemer.

Fig. 777.

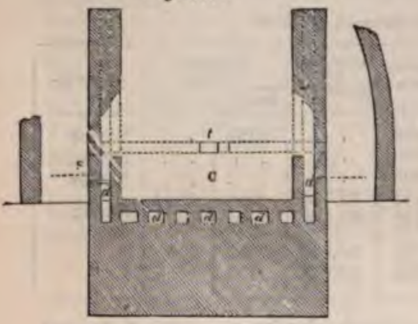


Fig. 778.

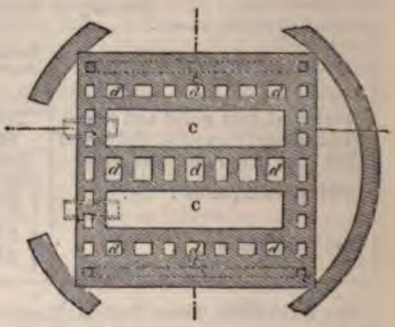
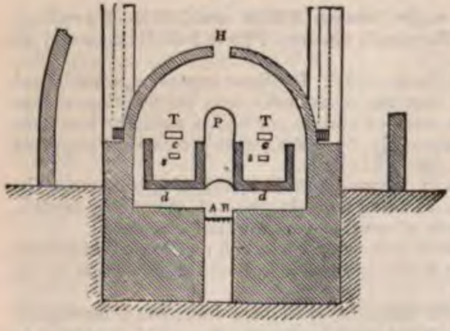


Fig. 779.



1. CARBURATION METHOD: *Cémentation.*—This method of producing steel is based upon the fact that, when malleable iron is heated in contact with charcoal or other carbonaceous substances, and without access of air, to a temperature somewhat below its melting-point, carbon is absorbed by the metal.

The iron used for producing steel in this way must be of the best quality, and free from the impurities which have already been mentioned as prejudicial to steel (see *ante*, p. 426). The *cement* or carburising material used is coarsely-powdered charcoal, sometimes mixed with horn-shavings, ferrocyanides, and similar substances.

The furnaces in which the operation is conducted, somewhat resemble glass-house furnaces, as shown by *figs.* 777, 778, and 779, and they are arranged so that a uniform temperature may be kept up in them for several days. The bars of iron are placed in the rectangular chambers C C, and imbedded in charcoal-powder. These *pots* (*caisses; Kasten*) are then closed with a layer of loam, and the heat gradually raised, during some three or four days, to the maximum degree, which is maintained two or three days longer, the progress of the operation being ascertained by drawing out a bar and testing it. When the conversion of the iron into steel is completed, the furnace is allowed to cool gradually, and the charge is taken out. The surfaces of the bars of steel are covered with numerous small blisters, for which reason it is called *Blister Steel* (*acier poule; Blasenstahl*).

The mode in which steel is produced by cementation is still but imperfectly understood. For a long time it was supposed that the iron combined directly with carbon in the solid state; but it is more probable that the conversion of the iron into steel is effected indirectly by gaseous carbon-compounds, such as carbonic oxide and hydrocarbons. At a sufficiently high temperature, carbonic oxide yields part of its carbon to iron, and is converted into carbonic acid, while marsh-gas and olefiant gas are decomposed in like manner by iron, yielding carburetted iron and hydrogen. Some years ago, Macintosh proposed to manufacture steel by heating bar-iron in an atmosphere of coal-gas; and, though this method has not come into use, good steel can be made by it, if the gas used for the purpose be free from sulphur. Animal charcoal, horn-shavings, ferrocyanides, &c., are sometimes mixed with the charcoal-powder used in producing steel by cementation, and these substances facilitate the conversion, chiefly by yielding gaseous carbon-compounds.

2. DECARBURATION METHODS.—In all these methods the abstraction of carbon from the cast-iron, and its conversion into steel, is effected by the oxidising action of atmospheric air, either directly or indirectly, through the medium of slags containing ferrous oxide, and the nature of the product depends very much upon the extent to which that action is allowed to continue.

a. Natural Steel is produced by melting white cast-iron (*Spiegeleisen*), or easily fusible grey cast-iron, with charcoal, in a finery-hearth or forge, and under a blast of air. This method of manufacture is restricted to countries where very pure cast-iron is obtained, by smelting spathic and magnetic iron-ores with charcoal. It is practised in Westphalia, Silesia, Styria, Carinthia, Sweden, and some other places, with a variety of modifications, arising chiefly from the nature of the cast-iron to be worked, or from other local circumstances. The process, however, is essentially the same in all cases, and differs from that already described as taking place in the conversion of cast-iron into malleable iron (iii. 345), only in so far that the decarburation is not carried to such an extent as in the manufacture of malleable iron.

β. Puddled Steel is produced, from such kinds of cast-iron as do not contain substances prejudicial to steel, by operating upon it, in reverberatory furnaces, in the same way that cast-iron is converted into malleable iron, but so as to effect only a less advanced decarburation.

γ. Bessemer Steel is produced by forcing atmospheric air into melted cast-iron. The carbon, being oxidised more readily than the iron, is converted into carbonic oxide, which escapes in a sufficiently heated state to take fire on coming in contact with atmospheric air. Considerable heat is generated by the oxidation of the carbon and iron, so that the temperature is kept above the melting-point of steel during the whole of the operation. When the decarburation has been carried far enough, the current of air is stopped, and a small quantity of white pig-iron, containing a large amount of manganese, is dropped into the liquid metal. This serves to facilitate the separation of any gas retained within the melted metal, which, after a few minutes' rest, is run into ingot-moulds.

The bars of blister-steel obtained by cementation are never uniform throughout their entire mass, the exterior portion being more highly carburised than the interior, and this difference is not always the same at all parts of the bars. To render them homogeneous, they are drawn out, while hot, under hammers or rollers, into thin bars, and a number of these bars are laid together in a *faggot* (*trousse; Garbe*), heated to a welding heat, and then hammered or rolled, this operation being repeated several times. The steel is then called *Shear Steel* (*acier raffiné; Gerbstahl*). The same operation has to be performed with the rough bars of natural steel, in order to render their texture uniform.

Steel, produced by either method, may be rendered still more homogeneous by melting it in a crucible, and running it into bars or ingots, *Cast Steel* (*acier fondu; Gussstahl*). Bessemer-steel, from the mode in which it is produced, is always of this kind.

The manufacture of cast-steel for various purposes has long been a very important branch of industry, and it is certain to become still more so, now that the new method of producing steel, introduced by Bessemer, admits of its being dealt with in very much larger masses than heretofore. It is, however, essential to the adoption of this method, to have at command cast-iron of good quality, and free from sulphur and phosphorus, which are so prejudicial to the quality of steel, and are not eliminated in the process of conversion, but are rather relatively increased in amount in the product obtained by the Bessemer method, when they are contained in the pig-iron operated upon. The growing importance of this method, and the rapid application of steel to new purposes, for which iron has hitherto been used, render it extremely desirable that a mode should be devised of smelting iron-ores, so as to prevent these deleterious substances from being retained in the pig-iron, or that some means of effecting their separation should be discovered. B. H. P.

STEINHEILITE. Syn. with DICHROÏTE.

STEINMANNITE. The name applied by Zippe to a mineral from Przibram in Bohemia, containing the sulphides of lead and antimony. It is, however, only galena contaminated with accidental admixtures.

STELLITE. Syn. with PECTOLITE.

STEPHANITE. *Brittle Silver-ore. Brittle Silver-glance. Black Silver. Brittle Sulphuret of Silver. Sprödglaserz. Sprödglanzerz.*—A sulphantimonite of silver occurring in trimetric prisms, homœomorphous with arragonite. Observed combinations: $oP . \infty P . \infty\breve{P}\infty , P . 2\breve{P}\infty$. Angle $\infty P : \infty P = 115° 39'$. Ratio of axes $a : b : c = 1 : 1{\cdot}5844 : 1{\cdot}0897$. Cleavage imperfect, parallel to $2\breve{P}\infty$ and $\infty\breve{P}\infty$. Twins are frequent, with plane of composition ∞P. The mineral also occurs massive, compact, and disseminated. Hardness = 2 to 2·5. Specific gravity = 6·299. Lustre metallic. Colour and streak iron-black. Fracture uneven. Sectile. Heated in an open tube, it melts and yields a sublimate of antimonious oxide, sometimes mixed with arsenious oxide. Before the blowpipe on charcoal it fuses somewhat readily, sometimes emitting an arsenical odour, to a dark-grey bead, which when heated in the reducing flame, either alone or with soda, yields a button of silver. It dissolves easily in warm nitric acid, with separation of sulphur and oxide of antimony.

Analyses: a. From Schemnitz (H. Rose, Pogg. Ann. xv. 474).—*b.* From Andreasberg (Kerl, Berg- u. hüttenm. Zeitung, 1853, No. 2):

	S.	Sb.	Ag.	Fe.	Cu.		
a.	16·42	14·68	68·54	. .	0·64	=	100·28
b.	16·51	15·79	68·38	0·14	. .	=	100·82

These analyses may be represented by the formula $6Ag^2S.Sb^2S^3$, requiring 15·6 per cent. sulphur, 14·0 antimony, and 70·4 silver.

Stephanite is a valuable ore of silver, occurring in veins with other silver-ores at Freiberg, Schneeberg, and Johanngeorgenstadt in Saxony, at Przibram and Ratieborzitz in Bohemia, at Schemnitz and Kremnitz in Hungary, at Andreasberg in the Hartz, at Zacatecas in Mexico, and in Peru. (Dana, ii. 86.)

STERCORITE. Herapath's name for sodio-ammonio-hydric phosphate, $Na(NH^4)HPO^4.4aq.$, found in the guano of Ichaboe (iv. 581).

STERNBERGITE. A sulphide of silver and iron, occurring at Joachimsthal in Bohemia, and at Schneeberg and Johanngeorgenstadt in Saxony, in tabular orthorhombic crystals, commonly implanted, and forming rose-like or fan-like aggregations. Angle $\infty P : \infty P = 119° 30'$; $oP : \bar{P}\infty = 121° 49'$. Axes: $a : b : c = 1 : 1{\cdot}7145 : 1{\cdot}4379$. Crystals sometimes compound, parallel to ∞P. Cleavage perfect, parallel to the base. The mineral is opaque, has a dark pinchbeck-brown colour, occasionally with a bluish-violet tarnish, and a semimetallic lustre; flexible in thin laminæ; very sectile; leaves traces on paper like plumbago. Hardness = 1 to 1·5. Specific gravity = 4·2 to 4·25. Before the blowpipe on charcoal it melts, with evolution of sulphurous anhydride, to a magnetic globule covered with silver; with borax it yields a globule of silver, and a glass coloured by iron. It dissolves in nitromuriatic acid with separation of sulphur. Contains, according to Zippe (Pogg. Ann. xxvii. 690), 33·2 per cent. silver, 36·0 iron, and 30·0 sulphur, agreeing approximately with the formula $(\tfrac{1}{3}Ag^2S.\tfrac{2}{3}Fe''S)^3.\overset{\prime\prime\prime}{Fe}{}^2S^3$, which requires 34·18 per cent. silver, 35·44 iron, and 30·38 sulphur.

STETHAL, or **STETHYLIC ALCOHOL.** $C^{18}H^{38}O = C^{18}H^{37}.H.O.$—The alcohol of the series $C^nH^{2n+2}O$, corresponding to stearic acid. It has not been obtained in the separate state, but occurs in spermaceti, together with ethal or cetylic alcohol ($C^{16}H^{34}O$), methal ($C^{14}H^{30}O$), and lethal ($C^{12}H^{26}O$). All these alcohols are separated together from the fatty acids of spermaceti, when that substance is saponified by alcoholic potash, in the manner described under CETYLIC ALCOHOL (i. 841), the ethal forming by far the largest portion of the alcoholic mixture. The presence of these several alcohols is manifested by their behaviour with potash-lime, by which they are converted into a mixture of palmitic acid (the principal portion), formed from ethol, stearic acid from stethal, myristic acid from methal, and lauric acid from lethal. When the ethal is crystallised several times from alcohol, till its melting-point is brought to 49°, a portion of the ethal, together wth the whole of the methal and lethal, remains in the mother-liquor, while the portion which crystallises out contains the stethal together with ethal. (Heintz.)

STIBETHYL, STIBMETHYL, &c. See ANTIMONY-RADICLES, ORGANIC (i. 339).

STIBILITE. *Stibiolite. Stiblite. Stibiconise.*—An oxide of antimony (formerly referred to antimony-ochre (i. 324), occurring at Losacio in Spain, Felsobanya and Kremnitz in Hungary, Goldkranach in Bavaria, and in the Carmen mine at Zacualpan in Mexico, forming masses of fine-grained to compact texture, sometimes porous and cracked, also pseudomorphs after stibnite (i. 329). Hardness = 5·5. Specific gravity = 5·78. Colour sulphur-, lemon-, or straw-yellow to yellowish-white; lustre waxy to dull; opaque; streak yellowish-white and shining. Reducible to antimony before the blowpipe with soda, but not alone. Contains, according to Delffs (J. pr. Chem. xl. 318), 75·83 per cent. antimony, 19·54 oxygen, and 4·69 water, agreeing approximately with the formula $Sb^2O^4.2H^2O$ (74·58 antimony, 19·83 oxygen, and 5·59 water).

STIBINE. A general name for antimony-bases formed on the type of ammonia, NH^3; thus SbH^3 is stibine; $Sb(C^2H^5)^3$ is ethylstibine, &c.

The same term is used by Beudant as a name of native antimonious sulphide; better called *Stibnite* or *Antimonite.*

STIBIOPHYLLITE. Syn. with Valentinite or native antimonious oxide.

STIBIOZINCYLS. The name given by Cooke to certain alloys of zinc and antimony. [See ZINC.]

STIBITE. A name of native antimonious oxide.

STIBIUM. The Latin name of Antimony.

STIBLITE. Syn. with STIBILITE.

STIBNITE. Native antimonious sulphide, Sb^2S^3.

STIBONIUM. Antimony-radicles formed on the type of ammonium, NH^4; thus $Sb(C^2H^5)^4$ is tetrethyl-stibonium.

STICK-LAC. See LAC (iii. 451).

STICTA PULMONACEA. A lichen formerly used as a remedy in diseases of the lungs. It contains a peculiar bitter principle, which, according to Weppen, is a white powder, slightly soluble in water and in ether, easily soluble in hot alcohol, forming a slightly acid solution which is precipitated by acids, acetate of lead, and silver-salts. Weppen (Pharm. Centr. 1838, p. 177) regarded this bitter substance as identical with cetrarin or cetraric acid (i. 839). According to Knop and Schnedermann (J. pr. Chem. xxxix. 363), the acid of *Sticta pulmonacea,* which they call stictic acid, is distinct from cetraric acid, though very much like it in composition and properties, and may be prepared in a similar manner; but it is less soluble in alcohol; the solution does not turn blue when boiled with hydrochloric or sulphuric acid, and stictate of potassium is less soluble than the cetrarate.

STIGMAPHYLLON. In the expressed juice of the tubers of *Stigmaphyllon jatrophæfolium,* a malpighiaceous tree indigenous in Brazil, De Luca and Ubaldini (Compt. rend. lix. 527) found a considerable quantity of asparagin.

STILBENE. $C^{14}H^{12}$. *Hydride of Stilbyl. Picramyl.* (Laurent, Rev. scient. xvi. 373.)—A hydrocarbon polymeric with benzylene (C^7H^6), obtained by heating sulphide of stilbene (hydride of sulphobenzoyl, i. 571). The compound melts, gives off sulphydric acid and sulphide of carbon; and on increasing the heat, stilbene passes over, first solidifying in scales, and afterwards thionessal:

$$\underset{\substack{\text{Hydride of}\\\text{Sulphobenzoyl.}}}{8C^7H^6S} \quad = \quad 2CS^2 \quad + \quad 3H^2S \quad + \quad \underset{\text{Stilbene.}}{2C^{14}H^{12}} \quad + \quad \underset{\text{Thionessal.}}{C^{26}H^{18}S}$$

To purify the stilbene, the first portions of the distillate are boiled with alcohol; the liquid is filtered to separate the thionessal, which is nearly insoluble in alcohol; and the liquid is left to cool. The stilbene is then deposited in crystals, which may be recrystallised from ether.

Stilbene may also be obtained from the crude product resulting from the action of sulphydrate of ammonium on oil of bitter almonds, the materials being left in contact for two or three weeks.

Stilbene crystallises in colourless nacreous plates belonging to the monoclinic system: observed combination $oP \,.\, \infty P \,.\, \infty P\infty$, the basal face oP predominating. Angle

$\infty P : \infty P = 53^\circ\, 30'$; $oP : \infty P = 100^\circ$; $\infty P : \infty P\infty = 116^\circ\, 45'$; $oP : \infty P\infty = 112^\circ$. The crystals are commonly joined together by the acute angles of the rhombuses. Stilbene is very slightly soluble in cold, but moderately soluble in boiling alcohol, more soluble in ether. It melts at a few degrees above 100°, boils at about 292°, and distils without alteration. Vapour-density = 8·4.

Stilbene dissolves in warm *fuming sulphuric acid*, and the solution saturated with baryta yields a soluble barium-salt of a conjugated acid. Stilbene is not decomposed by dilute *chromic acid*, but the concentrated acid decomposes it with violence when heated with it, converting it into benzoic hydride. With boiling *nitric acid* it yields several products, among which are nitrostilbene, $C^{14}H^{11}NO^2$—which is a yellow resinous substance,—and nitrostilbic acid, a yellowish powder nearly insoluble in water, soluble in alcohol, still more in ether, and apparently consisting of $C^{14}H^9(NO^2)O^4.2aq$.

When chlorine-gas is passed over fused stilbene, two isomeric compounds are formed, viz. chloride of stilbyl and hydrogen, $C^{14}H^{11}Cl.HCl$, and chloride of stilbene, $C^{14}H^{12}Cl^2$ (α and β chloride of stilbyl, according to Laurent). Both these compounds are crystalline; one of them is sparingly insoluble in ether, and nearly soluble in boiling alcohol; the other is easily soluble in alcohol, still more easily in ether. Both are resolved by alcoholic potash into two isomeric chlorides of stilbyl, or chlorostilbenes, $C^{14}H^{11}Cl$ (α and β chlorostilbase, according to Laurent), with simultaneous formation of chloride of potassium.

The *chlorostilbenes* α and β unite directly with 2 at. bromine, forming two isomeric compounds, $C^{14}H^{11}ClBr^2$, or perhaps $C^{14}H^{10}Br^2.HCl$, which dissolve in ether, and crystallise therefrom.

When stilbene is subjected to the prolonged action of chlorine, hydrochloric acid is evolved, and *trichloride of stilbyl*, $C^{14}H^{11}Cl^3$, or *dichloride of chlorostilbene*, $C^{14}H^{11}Cl.Cl^2$, is produced.

When bromine is poured upon stilbene, a white powder insoluble in ether is formed, consisting of *bromide of stilbene*, $C^{14}H^{12}Br^2$, or *bromide of stilbyl and hydrogen*, $C^{14}H^{11}Br.HBr$.

STILBENE, OXIDE OF. Laurent regarded benzoic hydride (bitter-almond oil) as the oxide of stilbene, $C^7H^6.O$.

STILBENE, PEROXIDE OF. Syn. with Stilbous Acid.

STILBENE, SULPHIDE OF. Syn. with Hydride of Sulphobenzoyl (i. 571).

STILBESE, PEROXIDE OF. Syn. with Stilbesic Acid.

STILBESIC ACID. *Acide Stilbeseux. Suroxide de Stilbèse.* (Laurent, J. pr. Chem. xxxv. 430.—Laurent and Gerhardt, Compt. chim. 1850, p. 117.)—A product obtained by treating crude bitter-almond oil (containing prussic acid) with chlorine-gas, assisting the action by heat towards the end. The whole then solidifies, on cooling, to a crystalline mixture of benzoic acid, stilbesic acid, a body crystallising in needles, and chloride of benzoyl; and if the chloride of benzoyl be allowed to drain on a funnel stopped with pounded glass, the mass pressed between paper, and treated with ether-alcohol, stilbesic acid remains behind, and may be crystallised by solution in boiling ether and spontaneous evaporation. It crystallises in monoclinic prisms, very slightly soluble in alcohol and ether, melting at 105°, and containing 71·60 per cent. carbon, and 4·33 per cent. hydrogen. Its solution in alcoholic ammonia yields, with silver-nitrate at the boiling heat, scales containing 48·7 per cent. silver. Hence Laurent deduced for the acid the formula $C^{28}H^{10}O^7$, and for the silver-salt $C^{28}H^8Ag^2O^7$; but its composition is very doubtful.

STILBIC ACID. Syn. with Benzilic Acid (i. 546).

STILBILIC or **STILBILOUS ACID.** Syn. with Stilbous Acid.

STILBIN. Syn. with Stilbene.

STILBITE. *Heulandite. Foliated Zeolite, Euzeolite.* A hydrated calcio-aluminic silicate, occurring in monoclinic crystals, which exhibit the combination $[\infty P\infty]$ $\infty P\infty . + 2P\infty . - 2P\infty . \infty P . oP - P . [P\infty]$; tabular from predominance of $[\infty P\infty]$. Ratio of axes $a : b : c = 2{\cdot}4785 : 1 : 1{\cdot}065$. Angle $b : c = 88^\circ\, 35'$; $\infty P : \infty P = 136^\circ\, 4'$; $oP : [P\infty] = 156^\circ\, 45'$. Cleavage perfect, parallel to the clinodiagonal. The mineral occurs also in globular forms, and granular. Hardness = 3·5 to 4·0. Specific gravity = 2·1 to 2·2. Lustre of $[\infty P\infty]$ pearly, of other faces vitreous. Colour various shades of white, passing into red, grey, and brown. Streak white. Transparent to subtranslucent. Fracture subconchoïdal to uneven. Brittle. Before the blowpipe it intumesces, melts, and becomes phosphorescent. Dissolves in hydrochloric acid, yielding slimy silica, but without gelatinising.

Analyses.—*a.* Faröe Islands (Thomson, *Outlines*, i. 347).—*b.* Iceland (Rammelsberg, *Mineralchemie*, p. 826).—*c.* Iceland (Damour, Ann. Min. iv. x. 207).—*d.* Berufjord, Iceland: crystallised; specific gravity = 2·175 (Waltershausen, Vulk. Gest. p. 252).—*e.* Nerbudda Valley, India: crystallised (Haughton, Jahresb. 1857, p. 676):

	a.	*b.*	*c.*	*d.*	*e.*
Silica . .	59·14	58·2	59·85	58·90	56·59
Alumina . .	17·92	17·6	16·15	16·81	15·35
Lime . .	7·65	7·2	7·55	7·38	5·88
Magnesia . .	. .	. .	. .	0·29	0·82
Soda . .	. .	. .	1·16	0·57	1·45
Potash . .	. .	. .	0·67	1·63	0·89
Water . .	15·40	16·0	14·33	14·32	17·48
Ferric oxide .	. .	. .	. .	0·12	
	100·11	99·0	99·71	100·02	98·46

These analyses are not very accordant, but the third and fourth may be nearly represented by the formula $Ca''O.Al^2O^3.6SiO^2.5$ aq., requiring 59·76 per cent. silica, 16·61 alumina, 9·06 lime, and 14·54 water. According to this formula, stilbite is very nearly related to brewsterite and epistilbite, the three minerals being represented by the formula $RO.Al^2O^3.6SiO^2 + 5$ aq., and the protoxide, RO, consisting, in stilbite, of lime with very little alkali; in epistilbite, of lime with a large proportion of soda; and in brewsterite, of strontia and baryta, with a small quantity of lime.

Stilbite occurs chiefly in amygdaloïdal rocks; also in gneiss, and occasionally in metalliferous veins. The finest specimens come from Iceland and the Faröe Islands, and from the Vendayah Mountains in Hindostan. Red varieties occur at Campsie in Stirlingshire, with desmin of the same colour, and brown in ore-beds at Arendal. It also occurs in the Kilpatrick Hills near Glasgow, in the Isle of Skye, in the Fassa Valley in the Tyrol, in the Hartz, and elsewhere; abundant in the amygdaloid of Abyssinia; occurs also at several localities in North America. (Dana, ii. 331.)

Beaumontite from Jones Falls, Maryland, is regarded by Dana and others as identical with stilbite; but the analysis (i. 524) agrees more nearly with the formula $R''O.Al^2O^3.8SiO^2 + 6$ aq.; moreover, according to Levy, the crystals belong to the dimetric system.

Desmin is a hydrated calcio-aluminic silicate, in which the ratio of the lime, alumina, and silica is the same as in stilbite; but the proportion of water is larger, and the crystals are trimetric. It was formerly called *stilbite* (the mineral just described under that name being then called *heulandite*); also *radiated zeolite*, *foliated zeolite*, *sphærostilbite*, and *hypostilbite*.

The crystals of desmin usually exhibit the combination $P \,.\, \infty\bar{P}\infty \,.\, \infty\breve{P}\infty$, like *fig.* 263 (CRYSTALLOGRAPHY, ii. 46), without $\breve{P}\infty$, but with oP. Axes $a : b : c$ = 0·9284 : 1 : 0·7558. Angle P : P in the brachydiagonal principal section = 119° 15′, in the macrodiagonal = 114° 0′; in the basal = 96°. Cleavage perfect, parallel to $\infty\breve{P}\infty$. It frequently occurs in sheath-like aggregations, and in globular, divergent, and radiated forms.

Hardness = 3·5 to 4. Specific gravity = 2·094 to 2·171. Lustre pearly on the faces $\infty\breve{P}\infty$ and the cleavage-faces, vitreous on the others. Colour white, occasionally yellow, brown, or red. Streak uncoloured. Subtransparent to subtranslucent. Fracture uneven. Brittle. Before the blowpipe it intumesces, and yields a milk-white bead. With acids it yields slimy silica, except Beudant's *sphærostilbite*, which yields a jelly.

Analyses of Desmin (Rammelsberg's *Mineralchemie*, p. 829).—*a.* Rödefjordshamm, in Iceland (Hauy's *stilbite dodecaèdre lamelliforme*), Hisinger.—*b.* Berufjord, Iceland (R. Weber).—*c.* Dalsmypen, Faröe Islands: *prehnitic stilbite* (Retzius).—*d.* Faröe Islands: so-called *sphærostilbite* (Beudant).—*e.* Gustafsberg in Jemtland (Sjögren).—*f.* Ilmen Mountains, near Miask: specific gravity = 2·19 (Hermann).—*g.* Andreasberg, in the Hartz (Karl).—*h.* Rienthal on the Gotthardstrasse, Canton Uri (G. Leonhard).—*i.* Pangelberg, near Nimptsch in Silesia (Zellner):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Silica . .	58·0	58·02	56·76	55·91	57·41	56·31	56·3	55·75	60·27
Alumina .	16·1	14·94	17·73	16·61	16·14	16·25	15·9	18·50	14·43
Lime . .	9·2	8·33	4·50	9·03	8·75	7·66	7·4	8·04	6·40
Soda . .	. .	. .	2·53	0·68	. .	1·03			
Potash . .	. .	1·30	. .	. .	. .	. .	0·6		
Water . .	16·4	17·71	18·33	17·84	16·60	17·75	17·6	17·00	18·50
Ferric oxide .	. .	. .	. .	. .	0·25	1·00	1·3	0·01	*0·21
	99·7	100·30	99·85	100·07	99·15	100·00	99·1	92·30	99·81

* Magnesia.

The greater number of these analyses may be represented by the formula $Ca''O.Al^2O^3.6SiO^2 + 6$ aq., requiring 58·09 per cent. silica, 16·14 alumina, 8·80 lime, and 16·97 water.

Of different composition are:—α. The so-called *Hypostilbite* from the Faröe Islands (Beudant); β. White and γ. Red desmin from Dumbarton in Scotland (Thomson):

SiO^2.	Al^2O^3.	CaO.	Na^2O.	H^2O.		
52·43	18·32	8·10	2·41	18·70	=	99·96
54·80	18·20	9·83	. .	19·00	=	101·83
52·50	17·32	11·52	. .	18·45	=	99·79

Desmin occurs mostly in cavities in amygdaloïd or trap. It is found also in some metalliferous veins, and in granite and gneiss. It is abundant in the Faröe Islands, in Iceland, and on the Isle of Skye in trap; at Andreasberg in the Hartz, and at Kongsberg and Arendal in Norway, with iron-ore; in the Vendayah Mountains, Hindostan, in large translucent crystals; in fine crystals, of a brick-red colour, in porphyritic amygdaloïd, near Kilpatrick in Dumbartonshire, &c. (Dana, ii. 833.)

STILBOUS ACID. $C^{15}H^{12}O^{3}$? A compound formed by treating crude bitter-almond oil with fuming sulphuric acid, or with chloride of sulphur (Laurent, Ann. Ch. Phys. [2], lxv. 193). When first prepared, it crystallises from ether or boiling alcohol in monoclinic prisms; but if kept for some time in the fused state, and then dissolved in alcohol, it crystallises in trimetric prisms. It melts at 360°; is insoluble in ammonia; is resolved by boiling caustic potash into benzoic acid and benzoic hydride; but when treated with very strong potash-ley, unites with the potash, forming a compound insoluble in strong, but soluble in dilute aqueous potash.

This compound was originally regarded by Laurent as *hydrate of benzoyl*, $C^{14}H^{5}O.HO$. It is sometimes regarded as identical with benzoate of benzoic hydride (i. 598), formed from crude bitter-almond oil, by the action of moist chlorine; but the identity of the two products is not satisfactorily established. All these compounds formed from crude bitter-almond oil require re-examination: for details respecting them, see *Gmelin's Handbook*, xii. 178.

STILBYL. $C^{14}H^{11}$. Stilbene may be regarded as the hydride of this radicle, $C^{14}H^{11}.H$.

STILLINGIA SEBIFERA. A euphorbiaceous plant, growing abundantly in the valleys of Chusan, the berries of which yield the fat called *Chinese vegetable tallow*. This fat appears to occur in several varieties.

a. Greenish-white; melts at 44·4°; yields, by saponification, an acid, which, after recrystallisation from alcohol, softens at 61·7°, melts at 67·8°, and forms a silver-salt containing 27·95 per cent. silver; probably a mixture of palmitic (margaric, according to Thomson and Wood) and stearic acids. (Thomson and Wood, Phil. Mag. [3] xxiv. 350; J. pr. Chem. xlvii. 239.)

b. The commercial tallow forms a light white mass, of specific gravity 0·818 at 12°, destitute of taste and odour (v. Borck). Has a faint odour, and turns brown on exposure to the air (Maskelyne). Melts at 37° (v. Borck, Maskelyne), solidifies partially at 32° (Maskelyne), 30° (v. Borck); and hardens at 22° (v. Borck), 26° (Maskelyne). The tallow recently melted and cooled again, melts at 44°; by expressing the more fusible portion, the melting-point of the residue may be raised to 49° (Maskelyne). The fat extracted from the husk by boiling alcohol melts at 40°, and after recrystallisation at 48° (v. Borck). It dissolves in oil of turpentine, and in coal-tar oil, in wood-spirit, ether, and alcohol, or in mixtures of these liquids; it dissolves partially at mean temperatures, completely at the boiling heat (Maskelyne). It has an acid reaction, arising from admixture of acetic or propionic acid. It contains olein and palmitin. (Maskelyne, Chem. Soc. Qu. J. viii. 1; v. Borck, J. pr. Chem. xlix. 395.)

STILLISTEARIC ACID. The name applied by v. Borck to the fatty acids obtained by saponification of Chinese tallow, which he supposed to have the composition $C^{15}H^{30}O^{2}$. Maskelyne has, however, shown that it is identical with palmitic acid.

STILLOLITE. Syn. with SILICIOUS SINTER.

STILPNOMELANE. A ferroso-aluminic silicate, occurring at Obergrund in Silesia, and in the Frederike mine, near Weilburg in Nassau, in foliated, radiated, and compact masses, having a specific gravity of 3—3·4; hardness 3—4; a lustre between vitreous and pearly on the cleavage-surface; black or greenish-black colour; and greenish streak. Dissolves imperfectly in acids.

Analyses.—*a*. Obergrund (Rammelsberg, *Mineralchemie*, p. 880).—*b*. Weilburg (Siegert):

	SiO^2.	AlO^3.	FeO.	CaO.	MgO.	KO.	H.	
a.	45·96	5·84	35·60	0·19	1·78	0·75	8·63	= 98·75
b.	45·07	4·92	37·78	1·67	0·94	. .	8·47	= 98·85

Some of the iron appears to be in the state of ferric oxide, but its quantity has not been determined with sufficient accuracy for the deduction of a formula.

STILPNOSIDERITE. A variety of native ferric hydrate, $Fe^2O^3.H^2O$, occurring massive, stalactitic, or incrusting, at Amberg in Westphalia, and two or three other localities. It has a black or blackish-brown colour; hardness = 4 to 5; specific gravity = 3·6 to 3·8.

STINKSTONE. A variety of limestone which emits a fetid odour when struck or rubbed (iii. 697).

STIRIAN. A name applied by Breithaupt to smaltine from Schladming in Styria.

STOÏCHIOMETRY. The law of chemical combination in definite proportions, and its application to chemical calculations.

STOLPENITE. A mineral from Stolpen, resembling bole in appearance, and containing, according to Rammelsberg (Pogg. Ann. xlvii. 180), 45·92 per cent. silica, 22·15 alumina, 24·86 water, and 3·90 per cent. lime, with traces of iron and magnesia.

STOLZITE. Native tungstate of lead. (See TUNGSTATES.)

STORAX. See BALSAMS (i. 497).

STRAKONITZITE. A pseudomorph after augite, occurring in the weathered gneiss of Mutenitz, near Strakonitz in Bohemia. It has a greenish-yellow colour, and specific gravity = 1·41. Contains, according to C. v. Hauer, 53·4 per cent. silica, 19·9 water, 15·4 ferrous oxide, 2·9 magnesia, 1·4 lime, and 7·0 alumina.

STRAMONIUM. See DATURA STRAMONIUM (ii. 307).

STRASS, or *Mentz Flux.* A kind of glass used in the preparation of artificial gems (ii. 841).

STRATIOTES ALOÏDES. *Water-soldier.*—This hydrocharidaceous plant yields, when dried, 17·2 per cent. ash, containing in 100 pts., according to Schulz-Fleeth (Pogg. Ann. lxxxiv. 98):

K^2O.	Na^2O.	CaO.	MgO.	Fe^2O^3.	SiO^2.	P^2O^5.	SO^3.	CO^2.	NaCl.
30·8	1·2	10·7	14·3	0·4	1·8	2·8	3·5	30·4	2·7

STRATOPEITE. A manganic silicate from Philipstad in Sweden. (SILICATES p. 259.)

STREAK OF MINERALS. Coloured mineral substances generally exhibit, when powdered, a lighter or, at all events, a different colour to that which belongs to them in mass: hence similarly coloured minerals may, in some cases, be distinguished one from the other by the colours of their powders. In order to see the colour, however, it is not necessary to pulverise the mineral, as it may be observed by scratching the mineral with a knife, or rubbing its edge on a rough white porcelain plate.

STROGANOWITE. An altered scapolite from the Sludänka river in Dauria (p. 203).

STROMEITE. Syn. with RHODONITE, or SILICIOUS MANGANESE (p. 107).

STROMEYERITE. Native argento-cuprous sulphide, or argentiferous copper-glance (p. 305).

STROMNITE. *Baryto-strontianite.*—A mineral from Stromness in the Orkneys, containing, according to Traill (Edinb. Phil. Trans. ix. 81), 27·5 per cent. sulphate of barium, 62·6 carbonate of strontium, and 2·6 carbonate of calcium, with 0·1 ferric oxide: probably a mechanical mixture.

STRONTIA, STRONTIAN. Oxide of strontium (p. 437).

STRONTIANITE. *Strontite. Strontites.*—Native carbonate of strontium. (See CARBONATES, i. 797.)

STRONTIANOCALCITE. A calcspar containing strontia, from Girgenti in Sicily. The crystals have the form and cleavage of ordinary calcspar, are grouped in spherical masses, colourless and transparent to white and translucent, and have a mother-of-pearl lustre.

STRONTIUM. *Symbol*, Sr. *Atomic weight*, 87·5.

The native carbonate of strontium, discovered, in 1787, at Strontian in Argyleshire, was at first regarded as carbonate of barium. Crawfurd's supposition, published in 1790, that this mineral contained a peculiar earth, was confirmed in 1792 by Hope (Edinb. Phil. Trans. iv. 3), and in 1793 by Klaproth. H. Davy, in 1808, first obtained from it the metal strontium.

Strontium occurs as sulphate in cœlestin, and as carbonate in strontianite; in small quantities in arragonite and brewsterite, and in very minute quantities in the mineral waters of Karlsbad and Kaiser-Franzensbrunnen, the salt-spring at Eger, &c., and in sea-water.

Preparation.—Strontium was first isolated by Davy in the same manner as barium (i. 500). Hare obtained it in a similar manner, and Clarke prepared it, in the same manner as barium, by heating strontia or the nitrate on charcoal in the oxyhydrogen-blowpipe flame. All these methods, however, yielded the metal in an impure state.

The pure metal is easily obtained by electrolysis of the fused chloride, in the manner given by Matthiessen (ELECTRICITY, ii. 438). Caron (Compt. rend. xlviii. 40) obtains it by fusing the chloride with an alloy of sodium and lead, tin, &c.; the reduction is not effected by sodium alone.

Properties.—Strontium has a yellow colour, like that of calcium, only a shade darker. Specific gravity = 2·5418. It oxidises in the air much more quickly than calcium. Its place in the electrolytic series, with water as the exciting liquid, is as follows:

$$\overset{+}{K},\qquad Na,\qquad Li,\qquad Ca,\qquad Sr,\qquad \overset{-}{Mg},\ \&c.$$

It burns like calcium, and acts similarly to it when heated in chlorine, oxygen, bromine, or iodine, or on boiling sulphur, or when thrown on water or acids. (Matthiessen.)

STRONTIUM, BROMIDE OF. $SrBr^2$.—The anhydrous bromide is obtained by evaporating and heating a solution of the carbonate in hydrobromic acid, also by burning strontium in bromine-vapour. It is a white mass, which melts without decomposition at a red heat. From the aqueous solution the bromide separates in long needles, containing $SrBr^2.3H^2O$, which do not effloresce in dry air, or even over oil of vitriol. When heated they melt in their water of crystallisation, and then give it off. The salt is easily soluble in water, somewhat soluble also in alcohol, and the alcoholic solution burns with a purple-red flame.

STRONTIUM, CHLORIDE OF. $SrCl^2$.—Produced when strontium burns in chlorine-gas; also, according to Weber (Pogg. Ann. cxii. 619), by heating anhydrous strontia in a stream of chlorine. It is usually prepared from cœlestin in the same manner as chloride of barium from heavy spar (i. 501). The crystallised chloride, $SrCl^2.3H^2O$, forms long deliquescent needles, which melt when heated, give off their water, and leave the anhydrous chloride in the form of a white enamel-like mass, or, according to Dumas, vitreous and transparent when perfectly pure. The anhydrous chloride absorbs 8 at. ammonia, whereby it is converted into a white powder. It dissolves easily in water; in 116·4 pts. cold and 262 pts. boiling alcohol of 99 per cent. (Fresenius.)

STRONTIUM, DETECTION AND ESTIMATION OF.—1. *Blowpipe Reactions.*—Strontium-compounds heated in the inner flame colour the outer flame carmine-red. An alcoholic solution of a strontium-salt burns with a carmine-red flame. The spectrum of strontium-vapour is characterised by a red line nearly coinciding with the solar line C, and a blue line between F and G (p. 380). All these reactions are distinctly perceptible in presence of a considerable quantity of barium-salt.

2. *Reactions in Solution.*—The reactions of strontium-salts closely resemble those of barium-salts. Sulphate of strontium, however, is somewhat more soluble than sulphate of barium: hence *sulphuric acid* or a *soluble sulphate* does not precipitate a dilute solution of a strontium-salt so quickly as it does that of a barium-salt. A barium-salt gives a precipitate with a solution of *sulphate of strontium*, which a strontium-salt of course does not. Strontium-salts are further distinguished from barium-salts by not forming precipitates with *silicofluoric acid* or *acid chromate of potassium*. A few drops of solution of strontium-chloride, evaporated on a watch-glass, yield needles of the hydrated chloride, whereas a solution of barium-chloride evaporated in like manner yields small cubes.

3. *Estimation and Separation.*—Strontium is best estimated as carbonate by precipitation with ammonium-carbonate and ammonia from a hot solution. The precipitation of strontium by this method is more complete than that of barium. Carbonate of strontium is not decomposed by ignition over an ordinary lamp. Strontium may also be estimated as sulphate; but as this salt is not absolutely insoluble in

water, it is necessary to add alcohol to complete the precipitation, which can only be done when the original strontium-salt is soluble in alcohol.

Strontium is separated from most other metals in the same manner as barium. When a solution previously freed from metals of the first and second groups (i. 217), by treatment with sulphydric acid and sulphide of ammonium, is further treated with carbonate of ammonium, the precipitate may contain the carbonates of barium, strontium, and calcium. From barium, strontium may be separated by dissolving the carbonates in a slight excess of hydrochloric acid; mixing the solution with excess of silicofluoric acid; then adding alcohol; leaving the whole to itself for twelve hours; filtering; washing the precipitate with weak spirit; and precipitating the strontium from the filtrate as sulphate. If the two metals are present as sulphates, it is best to treat the mixture repeatedly with a solution of potassic or ammonic carbonate without applying heat. The residue, when thoroughly washed and treated with dilute hydrochloric acid, leaves pure sulphate of barium, the whole of the strontium dissolving as chloride. (H. Rose, Pogg. Ann. xcv. 286.)

From calcium, strontium may be separated by the insolubility of its nitrate in absolute alcohol.

For the methods of separating strontium from barium and calcium together, see CALCIUM (i. 717).

For detecting small quantities of strontium (and barium) in calcareous minerals, Engelbach (Ann. Ch. Pharm. cxxiii. 255) subjects the pulverised carbonate, obtained by decomposing the natural sulphate or silicate, to strong ignition; then boils it thoroughly with distilled water, and evaporates the rapidly filtered solution with addition of hydrochloric acid—or, if alkali-metals are also present, precipitates with ammonia and carbonate of ammonium—and examines the chlorides or carbonates with the spectroscope.

4. *Atomic Weight of Strontium.*—Stromeyer in 1816 (Schw. J. xix. 228), by decomposing carbonate of strontium with nitric acid, and determining the quantity of carbonic anhydride evolved, estimated the atomic weight of strontium at 88·22. He further reported that, according to H. Rose's determination, 100 pts. chloride of strontium yield by precipitation 181·25 pts. chloride of silver. This gives (for $Ag = 108$, and $Cl = 35·5$) $Sr'' = 87·34$. Pelouze, in 1845 (Ann. Ch. Pharm. lvi. 204), by a similar method, found $Sr'' = 87·70$; and Dumas (*ibid.* cxiii. 34) found $Sr'' = 87·5$, which number may be taken as the correct atomic weight of the metal.

STRONTIUM, FLUORIDE OF, SrF^2, is prepared, like the corresponding barium-compound, by decomposing oxide or carbonate of strontium with hydrofluoric acid, or by precipitating a strontium-salt with fluoride of sodium. It is a white powder, insoluble in water and in aqueous hydrofluoric acid.

STRONTIUM, HYDRATE OF. See STRONTIUM, OXIDE OF.

STRONTIUM, IODIDE OF. SrI^2.—Obtained by saturating hydriodic acid with strontia or sulphide of strontium, and evaporating. It may be fused without decomposition in a closed vessel; but when heated in contact with the air, it gives off iodine, and is converted into strontia. It dissolves easily in water, and may be recrystallised therefrom.

STRONTIUM, OXIDE OF. SrO. *Strontia. Strontian.*—Prepared by heating the nitrate to redness, or by exposing the carbonate, either alone or mixed with charcoal, to the strongest heat of a forge-fire. It is a greyish-white porous mass, of specific gravity 3·0 to 4·0 (Davy), 3·932 (Karsten), infusible, not volatile, and glows in the blowpipe-flame with a dazzling white light. It has an alkaline taste and reaction. When moistened with water, it becomes hot, and falls to powder like lime; if only the exact quantity of water required be added, the strontia hardens to a crystalline hydrate. When heated nearly to redness in a stream of chlorine-gas, it glows brightly throughout its whole mass, and is converted into a sintered mass of chloride of strontium. (R. Weber, Pogg. Ann. cxii. 649.)

Hydrate or Hydrated Oxide of Strontium, $SrH^2O^2 = Sr''O.H^2O$, is produced, as just noticed, by the direct union of water with the anhydrous oxide. On dissolving this hydrate in 5 or 6 pts. of boiling water, filtering hot, and leaving the solution to cool slowly in a closed vessel, it deposits small, needle-shaped, transparent crystals, containing $SrH^2O.8H^2O$, which deliquesce on exposure to the air, and are ultimately converted into carbonate. When heated to 100° or above, they give off 50 per cent. water, and leave the monohydrate SrH^2O^2. By heating the crystals to low redness, the hydrate is obtained in the fused state, and solidifies on cooling to a greyish-white radiated mass. According to Bloxam (Chem. Soc. Qu. J. xiii. 48), hydrate of strontium gives off all its water at a red heat, leaving anhydrous strontia.

The crystals, $Sr''H^2O^2.8H^2O$, dissolve in 50 pts. of cold and 2·4 pts. of boiling water.

The solution, called *strontia-water*, is colourless, strongly alkaline, and absorbs carbonic acid from the air, becoming covered with a crust of carbonate. It may be prepared, like baryta-water, by boiling a solution of the sulphide with oxide of copper (i. 505).

A *peroxide of strontium* is obtained as a hydrate, in shining scales, by mixing strontia-water with peroxide of hydrogen. (Thénard.)

STRONTIUM, OXYSULPHIDE OF. See the next article.

STRONTIUM, SULPHIDES OF. The monosulphide, SrS, is prepared, like the corresponding barium-sulphide (i. 507), by reducing the sulphide with coal or charcoal. It is a white, granular, sintered but friable mass. By solution in a large quantity of boiling water, it is decomposed, the liquid, as it cools, yielding crystals of strontium-hydrate, whilst strontium-sulphydrate remains in solution:

$$2SrS + 2H^2O = SrH^2S^2 + SrH^2O^2.$$

If it be treated with a quantity of water not sufficient for this complete decomposition, a solution is formed containing chiefly sulphydrate of strontium, and on treating the residue with fresh quantities of water, a nearly pure solution of the hydrate is obtained. (H. Rose.)

Polysulphides (Schöne, Pogg. Ann. cxvii. 56).—By digesting 1 at. of the monosulphide and 3 at. sulphur in water, and leaving the solution to evaporate, at a temperature not exceeding 17°, a brownish-red viscid syrup is obtained, which at 8° solidifies to a crystalline mass of the tetrasulphide, SrS^4, with 6 at. water. This compound is very hygroscopic, soluble in water and in alcohol; on exposing the solutions to the air, hyposulphite of strontium is formed and remains dissolved, while sulphur and a small quantity of strontium-carbonate are deposited. On heating the syrup to 100°, or concentrating it under the air-pump at a temperature above 17° (best between 20° and 25°), the tetrasulphide separates with 2 at. water, as a light-yellow solid mass. When heated above 100°, it is decomposed by its water of crystallisation. It is not acted upon by carbonic disulphide.

By exposing the alcoholic solution of the tetrasulphide to the slow action of air, ruby-red, transparent, rhombic crystals are obtained, consisting of a hydrated oxytetrasulphide, $SrO.SrS^4.12H^2O$, which are decomposed by water. They are probably identical with the supposed disulphide, which Gay-Lussac obtained (Ann. Ch. Phys. [2] xiv. 362) by leaving a solution of strontium-sulphide to itself for some time.

Pentasulphide of strontium is formed by digesting the monosulphide in water with 4 at. sulphur, but exists in solution only. On evaporating the solution under the air-pump at about 20°, a residue is obtained consisting of the tetrasulphide mixed with sulphur. (Schöne.)

Sulphydrate of Strontium, $SrH^2S^2 = SrS.H^2S$.—Produced by passing sulphydric acid gas to saturation through strontia-water, or through water in which sulphide of strontium is suspended, or by dissolving sulphide of strontium in a small quantity of boiling water, whereby it is resolved, as above mentioned, into hydrate and sulphydrate. Berzelius, by evaporating in a vacuum the solution prepared by the first method, obtained the sulphydrate in large striated prisms, which when heated melt in their water of crystallisation, then give it off, together with sulphydric acid, and leave a residue of monosulphide of strontium. In other respects the compound exactly resembles sulphydrate of barium (i. 508).

STRUTHIIN. Syn. with Saponin (p. 192).

STRUVITE. Ammonio-magnesic phosphate, $(NH^4)\overset{\prime\prime}{Mg}{}^2(PO^4)^2.12aq.$, occurring in crystals in certain varieties of guano. (Phosphates, iv. 568.)

STRYCHNIC ACID. Syn. with Igasuric Acid (iii. 242).

STRYCHNINE. $C^{21}H^{22}N^2O^2$. (Pelletier and Caventou [1818], Ann. Ch. Phys. x. 142; xxvi. 44.—Pelletier and Dumas, Ann. Ch. Phys. xxiv. 176.—Liebig, *ibid.* xlvii. 171; xlix. 244.—Regnault, Ann. Ch. Phys. lxviii. 113.—Gerhardt, Revue Scientif. x. 192.—Nicholson and Abel, Chem. Soc. Qu. J. ii. 241.—Henry, Pharm. viii. 401.—Corriol, *ibid.* xi. 492.—Robiquet, *ibid.* xi. 580.—Wittstock, *Traité de Chimie de Berzelius.*—Henry, *fils*, J. Pharm. xvi. 752.—Gm. xvii. 479.)

This vegetable alkaloïd exists, together with brucine and igasurine, in nux-vomica, in St. Ignatius-beans, in the wood of *Strychnos Colubrina*, in *Strychnos Tieuté*, *Upas Tieuté*, and probably in several other varieties of *Strychnos* (see Brucine, i. 681). Java arrow-poison, found in a bamboo, contained 62 per cent. of strychnine.

Preparation: 1. *From St. Ignatius-beans.*—The rasped beans are exhausted with ether, and then treated several times with boiling alcohol. The alcoholic solution having been distilled to remove the alcohol, is to be treated with solution of hydrate of potassium to precipitate the strychnine (Pelletier and Caventou). This process is obviously imperfect.

2. *From Nux-vomica.*—*a.* The beans are exhausted with alcohol, and the solution is distilled to recover the alcohol. The residue is dissolved in water, and basic acetate of lead added until no further precipitation takes place. The strychnine remains in solution in the state of acetate; the liquid also contains colouring-matters, and the excess of basic acetate of lead. Sulphide of hydrogen is passed into the solution, which is then filtered, and boiled with magnesia. The precipitated strychnine, after being washed with water, is crystallised from alcohol. The mother-liquors retain the brucine. (Pelletier and Caventou.)

b. The pulverised nux-vomica is exhausted with boiling water, and the decoctions are evaporated until syrupy; powdered chalk is then added by degrees, until in slight excess. The precipitate contains the calcium-salt of an acid existing in nux-vomica, the strychnine, and other substances. After being washed, it is exhausted by treatment with alcohol of specific gravity 0·827, and the liquids are then evaporated in the water-bath to the crystallising-point. The strychnine is purified either by repeated crystallisations, or, better, by conversion into nitrate, and recrystallisation. The alkaloïd may be obtained from the nitrate by precipitation with ammonia. One kilogramme of nux-vomica yields by the above process 5 or 6 grammes of strychnine. (Henry.)

c. The following process is said to be more advantageous than the preceding ones: 1 kilogramme of nux-vomica is to be softened by being steamed, then dried, and pulverised moderately fine. It is then digested in the water-bath, with 4 or 5 litres of alcohol of specific gravity 0·856 acidified by 40 or 50 grammes of sulphuric acid. Quicklime is then added to the alcoholic solution, to remove the acid and precipitate the colouring-matter. The supernatant liquid is decanted, and the deposit is washed with alcohol. All the alcoholic liquors are then mixed, carefully filtered, and distilled. The residue in the still is coloured and alkaline; it is saturated with dilute sulphuric, hydrochloric, or acetic acid; and the solution is to be filtered, concentrated, and precipitated in the cold by a slight excess of ammonia. The precipitate is composed of a mixture of strychnine and brucine. It is to be digested with weak alcohol of specific gravity 0·942, to remove the brucine. The remaining strychnine is to be dissolved in alcohol of specific gravity 0·837, and the boiling solution treated with a small quantity of animal charcoal. The filtered solution, on cooling, deposits the strychnine in crystals. (Henry, *fils.*)

d. Eight pounds of the powdered nux-vomica are mixed with an equal weight of water, so as to form a thick paste, which is then exposed to a temperature of 20° to 25°. In the course of a few days, a violent fermentation sets in, which is generally finished in about eighteen to twenty days. The liquid is now pressed through a hair-sieve; the solid residue pressed, and boiled twice or three times with water; and the united liquids evaporated down to 12 quarts. To this 9 ounces of powdered quicklime are added, the whole left quiet for six or eight hours, and the liquid separated from the precipitate by pressure; it is then mixed with sulphuric acid, the calcic sulphate removed, and the liquid evaporated to 2 quarts. One ounce of lime is now added to it, and the treatment repeated as above described. The precipitate formed is submitted to great pressure, and united to the previous one. The dried precipitate is now digested with 2 quarts of alcohol of specific gravity 0·935, which dissolves out brucine and colouring matters; and from this solution strychnine is likewise obtained by crystallisation. The remaining precipitate is digested repeatedly with 6 quarts of alcohol of specific gravity 0·838, the solution filtered, and four-fifths of the alcohol recovered by distillation. In one or two days the strychnine separates as a white crystalline powder; it is washed several times with alcohol of specific gravity 0·935, to remove any adherent brucine, and is obtained perfectly pure by recrystallisation. (Molyn, J. Chim. méd. iii. 507.)

e. Nux-vomica is to be boiled with alcohol of 94 per cent. The liquid is to be decanted, and the residue dried in an oven; it then becomes easily pulverisable. The powder is to be exhausted with alcohol, and the liquids mixed. After being evaporated to a convenient bulk, acetate of lead is to be added as long as a precipitate is formed. Colouring matters, vegetable acids, and fatty substances are thus removed. The precipitate is thrown on a filter, and well washed; and the filtered liquor is evaporated until reduced to about a half or a third of the weight of the nux-vomica employed. Magnesia is then added to the liquor, and the whole is left at rest for several days, until the brucine has had time to deposit. The precipitate, having been collected on linen, is to be pressed, dried, and treated with alcohol of 83 per cent., to dissolve the alkaloïds. On distilling off the alcoholic liquors, the strychnine is first deposited, while the brucine remains in the mother-liquors. To purify the crude strychnine, it is to be saturated exactly with dilute nitric acid. On concentrating the solution, the nitrate of strychnine is first deposited, in needles, and the nitrate of brucine is afterwards deposited in much larger crystals. The last mother-liquors are gummy, but they still contain some of the alkaloïds, which must be extracted by a fresh treatment with magnesia, &c. as before. When brucine is precipitated, there always remains in solution a considerable quantity, which is deposited after a time in crystalline grains. One kilogramme of nux-vomica yields, on treatment as above, 2 grammes of nitrate of strychnine, and 2 grammes of nitrate of brucine. (Wittstock.)

3. *From Upas Tieutè.*—The filtered aqueous solution of the upas is digested with magnesia; the precipitate is washed, dried, and boiled out three times with alcohol; the alcoholic solutions are evaporated; the residue is dissolved in dilute sulphuric acid and digested with animal charcoal; and the solution is again precipitated by magnesia. The precipitate is then exhausted with alcohol, and the solution evaporated to dryness. (Pelletier and Caventou.)

Detection of Strychnine in cases of Poisoning (i. 127).

Properties.—Small, white, four-sided prisms, terminated by four-sided pyramids (Pelletier and Caventou). — Crystals of the trimetric or rhombic system. Lustre vitreous, pearly on the cleavage-faces. Hardness between 2 and 2·5 (Kengott, Pogg. xcv. 614). Crystals permanent in air, unaltered by light. Rotates polarised light to the left. May be fused without decomposition. Inodorous, taste intensely bitter. Excessively poisonous; one-eighth of a grain will kill a large dog; three-eighths of a grain cause in man violent tetanic, convulsive spasms of the extremities, trismus, opisthotonos, and other formidable symptoms; half a grain, given three times a day for several days, caused death with the usual symptoms. (Pereira, *Materia Medica*, ii. 1310.)

Strychnine in poisonous doses almost invariably produces tetanic convulsions. The smallest dose yet known to prove fatal, was in the case of Dr. Warner, who swallowed half a grain of sulphate of strychnine in mistake for morphia. In a few minutes he was seized with constriction of the throat, tightness of the chest, rigidity of the whole muscular system, and tetanic convulsions. He died in about fourteen minutes (*Taylor on Poisons*, p. 777). The writer has tried the effects of doses of one-twelfth of a grain, repeated every four hours. On the second day the effects were sufficiently unpleasant to render it proper to cease the experiment for a time. Great variation is found in the power of different individuals to resist the poison; doses of even three grains have been endured by patients, where the quantity has been very gradually increased (Gaz. méd., Mars 1845; *Taylor on Poisons*, p. 777). Strychnine has an alkaline reaction. It resists putrefaction, and may consequently be extracted successfully from bodies which have been buried for a long time, even after three years. (Macadam.)

Strychnine dissolves in 6667 parts of cold, and in 2500 parts of boiling water (Pelletier and Caventou.)

Decompositions.—1. Strychnine, when submitted to destructive distillation, yields pyrrol among other products (Grev. Williams). When cautiously heated, it gives off colourless vapours, probably of undecomposed strychnine, then melts to a brown liquid, which when further heated gives off brown vapours, and leaves a carbonaceous residue (Duflos). Strychnine by destructive distillation yields small quantities of chinoline (Gerhardt). Strychnine is very easily oxidised, at a red heat, by oxide of copper or chromate of lead, and therefore, contrary to the statements of many chemists, is very easily analysed by the ordinary processes (Abel and Nicholson). —2. Vapour of *iodine* acts on strychnine, forming a peculiar compound.—3. *Bromine* produces, in solutions of strychnine, a resinous precipitate of bromostrychnine (Laurent). —4. Dry *chlorine* does not act on strychnine or its salts, but chlorostrychnine is formed when the gas is passed into water in which strychnine is suspended. A solution containing 1 pt. of acetate of strychnine in 8,000 pts. of water is rendered turbid by *chlorine* (Marchand).—5. Solution of *chloride of lime* gives a white precipitate in dilute solution of acetate of strychnine (Horsley).—6. Strong *nitric acid*, if hot, converts the alkaloïd into a yellow explosive nitro-compound, which is probably nitrate of nitrostrychnine. The solution, on treatment with alkalis in excess, gives off volatile bases (Anderson). If strychnine turns red with cold strong nitric acid, it indicates the presence of brucine.—7. Cold *oil of vitriol* dissolves strychnine, forming a colourless solution, which yields coloured reactions with most oxidising substances. This solution yields the following reactions with various reagents:—*a. Peroxide of lead* gives a blue coloration, becoming violet, then red, and finally in a few hours yellow.—*b. Acid chromate of potassium* in the solid state, added to the above liquid on a porcelain plate, gives a fine violet coloration; if the quantity of strychnine present is large, the colour is pale-blue.—*c. Ferrocyanide of potassium* yields a somewhat similar reaction to *b*, but more permanent.—*d. Black oxide of manganese* affords a violet coloration, becoming dark-red in the course of an hour. The presence of santonin, or starch, does not prevent the recognition of strychnine by acid chromate of potassium in the above solution; sugar, quinine, or morphine renders it indistinct, but does not affect the reaction with peroxide of manganese. The presence of 30 pts. of tartar-emetic does not prevent the coloration with acid chromate of potassium, but 60 pts. render it indistinct. Very small quantities of animal matters, or vegetable extractive matters, render the above reactions indistinct, when the strychnine is present in minute traces only.—8. Hot solutions of *iodic acid* colour strychnine and its salts violet-red.—9. The iodides of the alcohol-radicles form derivatives which will be described further on.

Combinations.—With Iodine.—a. When a solution of 1 pt. of strychnine in 1 pt. of alcohol and 3 pts. of water is warmed with a little tincture of iodine, and left to cool spontaneously, crystals of an iodine-compound are deposited, having the properties of double absorption. Its formula is probably $C^{21}H^{22}N^2O^2.I^2$ (Herapath).—*b.* When a solution of strychnine in weak alcohol, acidified with hydrochloric or hydriodic acid, is precipitated with tincture of iodine, the precipitate dissolved in boiling alcohol, and the solution left to cool, bright red-brown prisms are formed permanent at 140°, and having the formula $C^{21}H^{22}N^2O^2.HI.I^2$. (Tilden.)

When 2 pts. of strychnine are triturated with 1 pt. of iodine, the resulting mass dissolved in boiling alcohol, and the solution concentrated and allowed to cool, laminæ are deposited having the colour of mosaic gold, and the formula $2C^{21}H^{22}N^2O^2I^3$.

STRYCHNINE SALTS.—Acids easily dissolve strychnine, forming neutral solutions having an intensely bitter taste, and virulently poisonous.

Acetates of Strychnine.—Neutral acetate of strychnine crystallises with difficulty, the acid salt easily. (Pelletier and Caventou.)

Arsenate of Strychnine, $2C^{21}H^{22}N^2O^2.3H^2O.As^2O^5 + H^2O$.—Monoclinic prisms, soluble in 15 pts. of cold, and in 5 pts. of hot water.

Arsenite of Strychnine, $2C^{21}H^{22}N^2O^2.H^2O.As^2O^3$.—Dull white cubes, efflorescing in the air.

Bromomercurate of Strychnine.—Formed in the same manner as the iodine-compound (*infra*), but using bromide instead of iodide of potassium.

Chloro-aurate of Strychnine, $C^{21}H^{22}N^2O^2.HCl.Au'''Cl^3$.—Lemon-yellow precipitate, very slightly soluble in water. Crystallises from alcohol in pale orange-coloured crystals. (Nicholson and Abel.)

Chromate of Strychnine, $2C^{21}H^{22}N^2O^2.H^2O.CrO^3$.—Lemon-yellow needles, neutral, and sparingly soluble in water and alcohol. (Nicholson and Abel.)

Chlorocadmiate of Strychnine, $2(C^{21}H^{22}N^2O^2.HCl).Cd''Cl^2$.—White glittering scales, long needles, or large transparent prisms. Does not lose water at 130°. (Galletly.)

Chloromercurate of Strychnine, $C^{21}H^{22}N^2O^2.HCl.Hg''Cl^2$.—A dense pulverulent precipitate, which soon turns gelatinous, is thrown down on adding solution of mercuric chloride to solution of hydrochlorate of strychnine. Crystallises from alcohol. (Nicholson and Abel.)

Strychnine with Mercuric Chloride, $C^{21}H^{22}N^2O^2.Hg''Cl^2$.—Thrown down by a solution of mercuric chloride from a solution of strychnine in weak alcohol. White crystalline precipitate, insoluble in water, alcohol, and ether. (Nicholson and Abel.)

Sulphate of Strychnine with Mercuric Chloride, $2C^{21}H^{22}N^2O^2.H^2SO^4.2Hg''Cl^2$.—Produced by dissolving the mercurous compound in sulphuric acid.

Strychnine with Mercuric Cyanide, $C^{21}H^{22}N^2O^2.Hg''Cy^2$.—An alcoholic solution of strychnine, precipitated by excess of solution of mercuric cyanide, yields this compound in small prisms, slightly soluble in water and alcohol, insoluble in ether. (Nicholson and Abel.)

Chlorate of Strychnine.—Strychnine dissolved in aqueous chloric acid forms a rose-red solution, which yields thin short prisms, and, when the solution is concentrated, solidifies completely.

Chloroplatinate of Strychnine, $2C^{21}H^{22}N^2O^2.2HCl.Pt^{iv}Cl^4$.—Solution of hydrochlorate of strychnine is precipitated pale-yellow by a solution of tetrachloride of platinum. The precipitate is nearly insoluble in water and ether, and with difficulty in boiling alcohol. From the latter solution it crystallises in scales resembling mosaic gold.

Chloropalladite of Strychnine, $2C^{21}H^{22}N^2O^2.2HCl.Pd''Cl^2$.—When a solution of dichloride of palladium is added to a solution of strychnine in hydrochloric acid, a brown flocculent mass is precipitated. It is soluble in water and alcohol, and from a boiling solution in the latter menstruum, may be obtained, on cooling, in dark-brown needles. It is not decomposed at 100°. (Nicholson and Abel.)

Hydrobromate of Strychnine, $C^{21}H^{22}N^2O^2.HBr$.—Produced by dissolving strychnine in hydrobromic acid, and crystallising from water. (Nicholson and Abel.)

Hydriodate of Strychnine, $C^{21}H^{22}N^2O^2.HI$.—A dense crystalline precipitate is thrown down on adding a solution of iodide of potassium to a solution of strychnine (v. Planta). The alcoholic solution, when evaporated, yields glassy four-sided needles. (Merck.)

Hydrochlorate of Strychnine, $C^{21}H^{22}N^2O^2.HCl$.—100 pts. of strychnine, when exposed to a current of hydrochloric acid gas, and then heated to 150°, retain 10·67 of hydrochloric acid (Regnault). The same salt is easily obtained by dissolving strychnine in hydrochloric acid. It is neutral towards vegetable colours (Nicholson and Abel). It rotates polarised light to the left; $[\alpha]_r = 28 \cdot 18°$. The salt is soluble in about 50 pts. of water at 22° (Bouchardat). (As to water of crystallisation, see Gm. xvii. 494.)

Hydrocyanate of Strychnine.—When strychnine is dissolved in aqueous hydrocyanic acid, and the solution is evaporated, the hydrocyanic acid is entirely expelled. (Pelletier and Caventou.)

Hydroferrocyanate of Strychnine, $4C^{21}H^{22}N^2O^2.H^4Fe''Cy^6.2H^2O$.—Colourless needles, produced by mixing cold saturated solutions of ferrocyanide of potassium and neutral salts of strychnine. (Brandis.)

Hydrofluate of Strychnine, $2C^{21}H^{22}N^2O^2.8HFl.H^2O$.—Colourless right rhombic prisms, having an acid reaction. (Elderhorst.)

Hyposulphite of Strychnine, $2C^{21}H^{22}N^2O^2.H^2S^2O^3.4H^2O$.—Formed in a mixture of strychnine, alcohol, and sulphide of ammonium on standing in the air. (How.)

Iodomercurate of Strychnine, $C^{21}H^{22}N^2O^2.HI.Hg''I^2$.—Obtained by mixing solutions of 2 at. hydrochlorate of strychnine, 6 at. iodide of potassium, and 1 at. mercuric chloride. Shining microscopic crystals, insoluble in cold and in hot water, and but little soluble in boiling alcohol. (Groves.)

Nitrate of Strychnine, $C^{21}H^{22}N^2O^2.HNO^3$.—Strychnine in fine powder is gently heated until dissolved with nitric acid, diluted until it is but feebly acid to the taste; the solution, on cooling, deposits beautiful colourless needles of nitrate of strychnine. If the nitric acid is too concentrated, the solution assumes a yellow colour immediately heat is applied, and a nitro-compound is formed. No acid nitrate is produced.

Mellitate of Strychnine.—When an alcoholic solution of strychnine is mixed with an alcoholic solution of mellitic acid, a dazzling white crystalline precipitate falls. It is soluble in 1500 pts. of cold, and in 650 pts. of boiling water; perfectly insoluble in alcohol. (Karmrodt.)

Oxalate of Strychnine.—*Neutral*, $2C^{21}H^{22}N^2O^2.C^2H^2O^4$. Oxalic acid neutralised with strychnine yields long flat needles, neutral to litmus.—*Acid salt*, $C^{21}H^{22}N^2O^2.C^2H^2O^4$. Obtained by treating the neutral oxalate with oxalic acid.

Perchlorate of Strychnine, $C^{21}H^{22}N^2O^2.HClO^4$.—A solution of sulphate of strychnine decomposed by perchlorate of barium yields small, pale-yellow, glassy, rhombic prisms.

Periodate of Strychnine.—Produced by dissolving strychnine in a warm aqueous solution of periodic acid; it crystallises in six-sided prisms terminated by four-sided pyramids.

Phosphantimonate of Strychnine.—Yellowish-white curdy precipitate, produced by adding a solution of phosphantimonic acid to a solution of a strychnine-salt.

Picrate of Strychnine.—An alcoholic solution of picric acid precipitates an alcoholic solution of strychnine pale-yellow; hot solutions, on cooling, yield fine yellow crystals.

Sulphate of Strychnine.—*Neutral*, $2C^{21}H^{22}N^2O^2.H^2SO^4$. Dilute sulphuric acid saturated with finely powdered strychnine (Nicholson and Abel) yields large four-sided prisms. The salt rotates polarised light to the left; $[\alpha]_r = 25 \cdot 58°$ for the salt dried at 40°.—*Acid*, $C^{21}H^{22}N^2O^2.H^2SO^4$. This salt is formed by adding diluted sulphuric acid to the neutral salt; it crystallises in long thin needles, and is very acid to test-paper. (Nicholson and Abel.)

Sulphocyanate, $C^{21}H^{22}N^2O^2.CyHS$.—Sulphocyanate of potassium throws down, from solutions of strychnine-salts, a dense crystalline precipitate; from hot solutions long silky needles. (Artus; v. Planta.)

Tartrates of Strychnine.—*Neutral dextrotartrate*, $2C^{21}H^{22}N^2O^2.C^4H^6O^6 + 4aq$. Tartaric acid is neutralised with strychnine. Efflorescent needles an inch long.—*Acid dextrotartrate.* Strychnine dissolved in excess of tartaric acid yields slender needles with acid reaction.

Antitartrate of Strychnine.—The *neutral salt* heated to 100° loses 7·8 per cent. water, and nothing more at 200°, but becomes coloured, but to a less extent than the dextrotartrate. The *acid salt* loses all its water of crystallisation (10·3 per cent.) more rapidly than the acid dextrotartrate.

Oxystrychnines, iii. 320.

DERIVATIVES OF STRYCHNINE.

Methylstrychnine, $C^{22}H^{24}N^2O^2 = C^{21}H^{21}N^2(CH^3)O^2$.—Finely-powdered strychnine is heated for some hours with slight excess of methylic iodide in a sealed tube. When the reaction is complete, the excess of methylic iodide is distilled off, and the residue is dissolved in hot water and filtered, to remove any uncombined strychnine. On cooling, the solution yields **crystals** of hydriodate of methylstrychnine, from which the base may be separated by means of oxide or sulphate of silver, as follows:—*a. By oxide of silver.*—The hydriodate, prepared as above, is agitated with 3 or 4 pts. of cold water and some oxide of silver, whereby iodide of silver is formed; the liquid then filtered off, and evaporated to the consistence of a syrup, whereupon it deposits crystals of hydrate of methylstrychnine. As the dark mother-liquor cannot be made to crystallise, the following process may be substituted:—*b.* The solution of hydriodate of methylstrychnine is to be decomposed with an equivalent quantity of sulphate of silver; the solution separated from the iodide of silver is mixed with baryta-water, and evaporated to dryness; and the residue is heated with water, and evaporated: crystals of hydrate of methylstrychnine then separate out. As the salt thus obtained contains excess of water, it is to be dried between 130° and 140°. (For very full details concerning the reactions and decompositions of methylstrychnine, see Gm. xvii. 507.)

It is remarkable that hydrate of methylstrychnine is not poisonous. Rabbits can take 11 grains in the course of a day without being poisoned (Stahlschmidt). Hydrate of methylstrychnine forms easily soluble and crystalline salts with acids. Aqueous methylstrychnine precipitates salts of nickel, cobalt, iron, and copper; it also precipitates alum, but an excess does not redissolve the precipitate.

Phosphate of Methylstrychnine, $C^{21}H^{21}N^2(CH^3)O^2.PH^3O^4$.—Aqueous methylstrychnine neutralised with phosphoric acid yields a crystalline mass, readily soluble in water and alcohol. (Stahlschmidt.)

Sulphate of Methylstrychnine.—a. Neutral, $2C^{21}H^{21}N^2(CH^3)O^2.H^2SO^4$.—*Preparation* (see Methylstrychnine, *b*). May also be obtained by neutralising the aqueous base with dilute sulphuric acid. Thin pearly laminæ, efflorescent, easily soluble in water.—*b. Acid salt,* $C^{21}H^{21}N^2(CH^3)O^2.H^2SO^4$. Crystallises easily in laminæ, which have a strongly acid reaction. (Stahlschmidt.)

Hydriodate of Methylstrychnine, $C^{21}H^{21}N^2(CH^3)O^2.HI$. Pearly laminæ, requiring 212 pts. of cold, but easily soluble in hot water. Difficultly soluble in alcohol. (Stahlschmidt.)

Hydrobromate of Methylstrychnine, $C^{21}H^{21}N^2(CH^3)O^2.HBr$.—Thrown down when bromide of potassium is added to a strong solution of the hydrochlorate. Sparingly soluble in cold, but easily in hot water. (Stahlschmidt.)

Hydrochlorate of Methylstrychnine, $C^{21}H^{21}N^2(CH^3)O^2.HCl$.—Formed by neutralising the base with hydrochloric acid, or decomposing the sulphate with chloride of barium. Fine prisms half an inch long, soluble in water and alcohol.

Chloroplatinate of Methylstrychnine.—Pale-yellow precipitate, difficultly soluble in water and alcohol, insoluble in ether.

Ethylstrychnine, $C^{23}H^{26}N^2O^2 = C^{21}H^{21}N^2(C^2H^5)O^2$.—*Preparation.* Similar to that of methylstrychnine, but substituting ethylic for methylic iodide. The base may be precipitated by ether from the solution filtered from oxide of silver.

Carbonates of Ethylstrychnine.—a. Neutral. When moist carbonate of silver is agitated with hydriodate of ethylstrychnine and water, a colourless solution is obtained, which, evaporated in a vacuum, or at 100°, leaves a crystalline residue. Water dissolves carbonate of ethylstrychnine, leaving flocks of a new base (How).—*b. Acid,* $C^{21}H^{21}N^2(C^2H^5)O^2.H^2CO^3$.—When carbonic acid is passed into the solution of the neutral carbonate, and the filtrate is evaporated *in vacuo*, or at 100°, a white crystalline mass is formed, having an alkaline reaction. It dissolves in absolute alcohol, and is precipitated from the solution by ether in colourless prisms. (How.)

Hydriodate of Ethylstrychnine, $C^{21}H^{21}N^2(C^2H^5)O^2.HI$.—Shining white four-sided prisms. (How.)

Nitrate of Ethylstrychnine, $C^{21}H^{21}N^2(C^2H^5)O^2.HNO^3$.—Prepared by decomposing the hydriodate with nitrate of silver. Colourless, highly refractive prisms, only slightly soluble in cold, easily in boiling water. (How.)

Chloroplatinate of Ethylstrychnine, $2C^{21}H^{21}N^2(C^2H^5)O^2.2HCl.Pt^{iv}Cl^4$.—Yellow precipitate, which becomes crystalline in a few hours. (How.)

Amylstrychnine, $C^{21}H^{21}N^2(C^5H^{11})O^2$.—Prepared, like ethylstrychnine, by acting with moist oxide of silver on the hydrochlorate of amylstrychnine. (How.)

Hydrochlorate of Amylstrychnine, $2[C^{21}H^{21}N^2(C^5H^{11})O^2.HCl]H^2O$.—Prepared by heating, for 100 hours, finely-powdered strychnine with chloride of amyl. Colourless, oblique, rhombic prisms. (How.)

Nitrate of Amylstrychnine, $C^{21}H^{21}N^2(C^5H^{11})O^2.HNO^3$.—Prepared by decomposing hydrochlorate of amylstrychnine with nitrate of silver. Radiated groups of colourless needles.

Compounds produced by the action of Dibromide of Ethylene on Strychnine.

Dihydrobromate of Ethylene-strychnine, $C^{21}H^{20}N^2(C^2H^4)O^2.2HBr$.—When strychnine is heated in a sealed tube for a quarter of an hour, with alcohol and excess of dibromide of ethylene, and the resulting crystals are boiled with water until the alcohol and excess of dibromide of ethylene are expelled, the solution, on standing, deposits crystals of this salt. White crystals, only slightly soluble in cold, but easily in hot water and alcohol. The solution is not precipitated by ammonia, potash, or soda. The crystals, treated with acid chromate of potassium and sulphuric acid, yield the same reaction as strychnine (Ménétriès). Treated with silver-salts, the crystals give up half their bromine, but moist oxide of silver removes the whole; thus two series of compounds are formed.

a. Compounds containing Bromine.—An aqueous solution of the crystals is precipitated by sulphate of silver; the excess of silver, and also of sulphuric acid, is removed by baryta-water; carbonic acid is then passed in, and the solution is filtered: the resulting alkaline liquid, evaporated to dryness, leaves a resin, which Ménétriès calls *Hydrated Oxide of Strychnine-bromethyl-ammonium*, and represents by the formula $C^{21}H^{21}N^2(C^2H^4Br)O^2.H^2O$.

Sulphate of Strychnine-bromethyl, $C^{21}H^{21}N^2(C^2H^4Br)O^2.H^2SO^4$.—Obtained by decomposing dihydrobromate of ethylene-strychnine with sulphate of silver.

Nitrate of Strychnine-bromethyl, $C^{21}H^{21}N^2(C^2H^4Br)O^2.HNO^3$.—Obtained by decomposing dihydrobromate of ethylene-strychnine with nitrate of silver. White needles, sparingly soluble in cold, readily in hot water, not decomposed by alkalis.

Platinum-salt, $2C^{21}H^{21}N^2(C^2H^4Br)O^2.2HCl.Pt^{iv}Cl^4$.—Obtained by precipitating the dihydrochlorate with tetrachloride of platinum.

b. Compounds free from Bromine:—

Hydrate of Ethylene-strychnine, $C^{21}H^{20}N^2(C^2H^4)O^2.H^2O$.—Solution of dihydrobromate of ethylene-strychnine, digested with moist oxide of silver, becomes of a reddish colour, and the hydrate is obtained by evaporating the filtered solution. (Ménétriès.)

Trichlorethylene-strychnine, $C^{21}H^{17}Cl^3N^2(C^2H^4)O^2$. — A white frothy substance, obtained by passing chlorine into an aqueous solution of hydrate of ethylene-strychnine. (Ménétriès.)

Nitrate of Nitro-ethylene-strychnine, $C^{21}H^{19}(NO^2)N^2(C^2H^4)O^2.HNO^3$. — When an aqueous solution of hydrate of ethylene-strychnine is mixed with nitric acid, a white crystalline powder is deposited, insoluble in water, but soluble in strong acids; on evaporation with nitric acid, an orange-red substance is formed, which has probably the above formula.

Chlorostrychnine, $C^{21}H^{21}ClN^2O^2$.—When a hot solution of hydrochlorate of strychnine is treated with chlorine-gas, a resin gradually deposits, the solution retaining hydrochlorate of chlorostrychnine. Ammonia is then added to the solution drop by drop, until a small permanent precipitate is formed, the liquid is filtered, and the filtrate is precipitated with ammonia. (Laurent.)

Sulphate of Chlorostrychnine, $2C^{21}H^{21}ClN^2O^2.H^2SO^4$.—Prepared by neutralising dilute sulphuric acid with chlorostrychnine, and obtained in crystals by evaporating the solution.

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STRYCHNINE-SALTS.—*Salts generally:* Nicholson and Abel, Chem. Soc. Qu. J. ii. 241.—*Arsenite:* Chiappero, N. Br. Arch. cxv. 94.—Ceresoli, N. J. Pharm. [4], i. 343.—*Betuloretinate:* Kosmann, J. Pharm. [3], xxvi. 204.—*Carbonate:* Langlois, Ann. Ch. Phys. [3], xlviii. 502.—*Chlorocadmiate:* Galletly, Ed. New Phil. J. iv. 94.—*Chlorozincate:* Gräfinghoff, J. pr. Chem. xcv. 229.—*Hydrochlorate of Strychnine and Cyanide of Mercury:* Köhl and Swoboda, Chem. Gaz. 1863, p. 70.—*Hydrosulphocyanate:* Artus, J. pr. Chem. iii. 320; viii. 253.—Henry, J. Pharm. xxiv. 194.—Lepage, J. Pharm. xxvi. 140.—Dollfus, Ann. Ch. Pharm. lxv. 215.—*Hydroplatinocyanate:* Schwarzenbach, Pharm. Viertelj. viii. 518.—*Iodate:* Serullas, Ann. Ch. Phys. xlv. 275.—*Periodate:* Bödeker, Ann. Ch. Pharm. lxxi. 64.—*Iodomercurate:* Groves, Chem. Soc. Qu. J. ii. 97.—*Hydrofluate:* Elderhorst, Ann. Ch. Pharm. lxxiv. 77.—*Hyposulphate:* How, Pharm. Centr. 1855, p. 95.—*Hippurate* and *Oxalurate:* Ann. Ch. Pharm. lxxiv. 77.—*Mellitate:* Karmrodt, Ann. Ch. Pharm. lxxxi. 170.—*Oxalates:* Elderhorst, loc. cit.—*Tartrates:* Arppe, J. pr. Chem. liii. 331.—Pasteur, Ann. Ch. Phys. [3], xxxviii. 437.—Stenhouse, Ann. Ch. Pharm. cxxix. 25.

Iodo-compounds.—Tilden, Chem. Soc. J. [2], iii. 99.—Herapath, Chem. Gaz. 1855, p. 320; Proc. Roy. Soc. June 1856.

Benzoic derivatives of Strychnine.—Schützenberger, Compt. rend. xlvii. 233; Chem. Gaz. 1858, p. 387.

SUBSTITUTION-COMPOUNDS OF STRYCHNINE.—*Methylstrychnine:* Stahlschmidt, Pogg. Ann. cviii. 513.—*Ethylstrychnine:* How, Trans. Roy. Soc. Edin. xxi. 1, 27; Chem. Gaz. 1854, pp. 321, 341, 365.—*Amylstrychnine:* How, loc. cit.—*Compounds produced by the action of Dibromide on Ethylene:* Ménétriès, J. pr. Chem. lxxxv. 230.

Crystalline form of some Salts.—Descloizeaux, Compt. rend. xliv. 909.

C. G. W.

STRYCHNOCHROME or **STRYCHNOCHROMIN.**—A resinous yellow colouring matter, from the lichens of false Angustura, also from those found on the bark of *Strychnos Pseudochina*, as well as from *Upas Tieuté*. The lichens are exhausted with ether, and then with alcohol; the alcoholic tincture is evaporated; and the residue is boiled repeatedly with water, which dissolves extractive matters, and leaves the yellow. It is a reddish-yellow, tasteless, non-poisonous powder. It dissolves in strong nitric acid with fine green colour, which disappears on diluting the solution with water; but appears again when the liquid is concentrated, and is turned yellow by sulphuric acid and ferrous sulphate. Strong nitric acid also throws down from alcoholic strychnochrome a green precipitate, which loses its colour when washed. Oil of vitriol turns strychnochrome green; strong caustic potash decomposes it.—It is nearly insoluble in boiling water and dilute alkalis; soluble in acetic acid, from which it is precipitated by alkalis; easily soluble, with reddish-yellow colour, in alcohol; and very slightly soluble in ether and volatile oils. (Pelletier, J. Pharm. v. 546.—Pelletier and Caventou, Ann. Ch. Phys. [2], xxvi. 54.)

The strychnine prepared from *Nux-vomica*, *Faba St. Ignatii*, and *Upas Tieuté* obstinately retains a yellow colouring-matter, which remains in solution when an aqueous extract of the upas is precipitated with magnesia, and is obtained as a yellow extract on evaporation. This body is coloured bright-red by strong nitric acid; it dissolves easily in water and alcohol, and is not precipitated by neutral acetate of lead. (Pelletier and Caventou.)

STRYCHNOS. A genus of apocynaceous plants, including several species which yield strychnine and brucine. *Strychnos colubrina*, a tree growing in the Moluccas, yields snake-wood, which contains a large quantity of fatty matter, and, according to Pelletier and Caventou, a certain quantity of strychnine, but less than nux-vomica; it was formerly used as an antidote to the bites of poisonous serpents. The fruit of *Str. Nux-vomica* yields strychnine and brucine. *Str. St. Ignatii* yields the beans of St. Ignatius, which contain strychnine with a very small quantity of brucine. *Str. Tieuté* yields Upas-tieuté, the Javan arrow-poison, which also contains strychnine with traces of brucine. The bark of *Str. Pseudochina*, a tree growing in Brazil, and used there as a febrifuge, is said by Vauquelin not to contain strychnine.

STUDERITE. A fahl-ore occurring in the dolomite of Ausserberg, in the Valais. It is laminar to massive, of uneven fracture, black, of specific gravity 4·65. According to an analysis by Fellenberg (Jahresb. 1865, p. 872), it contains, in 100 parts:

S.	Sb.	As.	Bi.	Cu.	Zn.	Fe.	Pb.	Ag.
24·47	15·58	11·49	0·58	38·17	5·11	2·76	0·88	0·96

STÜBELITE. A mineral found in the island of Lipari, and analysed by A. Stübel (Jahresb. 1865, p. 892). It is amorphous, botryoïdal, kidney-shaped, or encrusted; very brittle, of conchoïdal fracture, and velvet-black to pitch-black colour. Hardness = 4 to 5. Specific gravity = 2·223 to 2·263. Contains:

SiO^2.	Al^2O^3.	Fe^2O^3.	Mn^2O^3.	MgO.	CuO.	Cl.	H^2O.		
26·99	5·37	10·18	21·89	1·03	15·23	0·77	15·85	=	98·31

STYLOBITE. Syn. with GEHLENITE.

STYLOLITES. Peculiar elongated calcareous formations, occurring in the Muschelkalk at Rüdersdorf, near Berlin.

STYLOTYPE. An antimonial fahl-ore from Copiapo in Chile, occurring in groups of four-sided nearly rectangular prisms, probably belonging to the trimetric system. It has an imperfectly conchoïdal fracture, iron-black colour, and black streak. Hardness = 3. Specific gravity = 4·79. Contains:

S	Sb.	Cu.	Ag.	Fe.	Pb, Zn.		
24·30	30·53	28·00	8·30	7·00	trace	=	98·13

agreeing nearly with the formula $3\left\{\begin{matrix}(Cu^2;\ Ag^2)\frac{2}{3} \\ Fe\frac{1}{3}\end{matrix}\right\}.Sb^2S^3$, which is of the general form $3R''S.Sb^2S^3$.

STYPHNIC ACID. Syn. with OXYPICRIC ACID (iv. 317).

STYPTERITE. Native hydrated sulphate of aluminium. (See SULPHATES.)

STYPTICITE. Native basic ferric sulphate. (See SULPHATES.)

STYRACIN. Styrylic or Cinnylic Cinnamate, $C^{18}H^{16}O^2 = \left.\begin{matrix}C^9H^7O \\ C^9H^9\end{matrix}\right\}O$. (i. 986.)

STYRACOL.
STYRACONE. } Syn. with STYRYLIC ALCOHOL (p. 447).

STYRAX. Syn. with STORAX (i. 497).

STYROL. Syn. with CINNAMENE, C^8H^8 (i. 982).

Distyrol, $C^{16}H^{16}$, is produced by heating cinnamic acid with aqueous hydrobromic acid of specific gravity 1·12, or with a mixture of 1 pt. oil of vitriol and 2 pts. water:

$$2C^9H^8O^2 = 2CO^2 + C^{16}H^{16}.$$

It is an oily hydrocarbon, which forms with bromine the crystalline compound, $C^{16}H^{16}Br^2$. It is not converted into metastyrol (metacinnamene, i. 982) by continued heating to 200°. (Erlenmeyer, Ann. Ch. Pharm. cxxxv. 122.)

STYRONE. Syn. with STYRYLIC ALCOHOL.

STYRYL. Syn. with CINNYL, C^9H^9.

STYRYLAMINE. $C^9H^{11}N = N\left\{\begin{matrix}C^9H^9 \\ H^2\end{matrix}\right.$. *Cinnylamine.* (Ramdohr, Zeitschr. f. Pharm. 1858, p. 113; Jahresb. 1858, p. 448.)—A base, produced by heating styrylic chloride with a solution of ammonia in absolute alcohol in sealed tubes to 100° (the tubes are apt to explode at higher temperatures). The resulting hydrochlorate of styrylamine is purified by recrystallisation from water and pressure between paper; and from the aqueous solution of this salt, the base is separated by potash as a bulky precipitate, which, by solution in ether and spontaneous evaporation, is obtained in small colourless crystals.

Styrylamine melts easily to a yellow oil, which volatilises at 100°. The vapours, as well as the ethereal solution, are alkaline. It has a bitter, caustic, very persistent taste, and dissolves readily in ether. The aqueous solution exhibits the following reactions:—With the *nitrates of barium, calcium*, and *magnesium*, in neutral solution, white precipitates; with *ferric chloride*, a brown-red, rather dense precipitate; with *zinc-sulphate*, white, insoluble in excess of the alkali; with *cupric sulphate* and *nickel-sulphate*, greenish-white, insoluble in excess; with *lead-acetate*, white; with *mercuric chloride*, white, bulky; with *silver-nitrate*, no reaction; with *auric chloride*, immediate yellowish-red precipitate; with *platinic chloride*, egg-yellow; with *potassic permanganate*, copious brown precipitate; with *potassic chromate* and *sulphuric acid*, reduction of the chromic acid to chromic oxide; with *potassic sulphocyanate*, slight crystalline precipitate after some time; with *tannin*, an immediate precipitate.

Hydrochlorate of Styrylamine, $C^9H^{11}N.HCl$, crystallises from water in stellate groups of snow-white crystals, belonging to the regular system. The *chloroplatinate*, $2C^9H^{11}N.H^2Cl^2.Pt^{iv}Cl^4$, is an egg-yellow precipitate, sparingly soluble in cold, more easily in hot water, insoluble in alcohol and ether; when heated it melts, blackens, gives off strong-smelling vapours, and leaves a large quantity of charcoal.

STYRYLIC ALCOHOL. $C^9H^{10}O = \left.\begin{matrix}C^9H^9\\H\end{matrix}\right\}O$.—An alcohol produced by distilling styracin (styrylic cinnamate) with caustic potash or soda;—already partly described as CINNYLIC ALCOHOL (i. 992). According to Ramdohr (Zeitschr. f. Pharm. 1858, p. 113; Jahresb. 1858, p. 446), the distillation should be conducted in copper vessels, because glass vessels are liable to be broken by the percussive ebullition, caused by the separation of the alkaline cinnamate produced. The styrylic alcohol passes over with the aqueous vapour, and separates on the water, in the course of a few days, in fine crystals (or, in warm weather, sometimes as an oil, which may remain liquid for a long time). It is somewhat soluble in cold water, less soluble in a strong solution of common salt.

Styrylic alcohol is converted by oxidation into cinnamic aldehyde, C^9H^8O, and cinnamic acid, $C^9H^8O^2$. When poured in the fused state on *platinum-black*, it is converted, after a few days, almost wholly into cinnamic aldehyde (Strecker).—With *chromic acid*, or a mixture of potassic chromate and sulphuric acid, it becomes hot, and yields cinnamic acid, which separates on the surface, and if the liquid be boiled, is further converted into benzoic aldehyde (bitter-almond oil) (Wolff).—Heated with strong *potash-ley* and *peroxide of lead*, it gives off a large quantity of benzoic aldehyde, and the residue contains cinnamic acid; the peroxide of lead is, at the same time, reduced to protoxide, or sometimes even to metal (Wolff).—With *potash and carbonic disulphide*, it yields a salt analogous to xanthate of potassium (Scharberg).—When heated with *nitric acid*, it dissolves, and is slowly attacked, a large quantity of nitrous acid being evolved, benzoic aldehyde distilling over, and benzoic acid remaining behind. If the formation of nitrous acid be prevented by addition of urea, a smaller quantity of benzoic aldehyde is formed, and the residue contains nitro-cinnamic acid. (For the other reactions see the next article.)

STYRYLIC ETHERS. (Ramdohr, *loc. cit.*)—*Styrylic Acetate*, $C^2H^3(C^9H^9)O^2$, is produced by the action of acetic chloride on the alcohol; it distils without decomposition.—*Styrylic Benzoate*, $C^7H^5(C^9H^9)O^2$, produced in like manner is crystalline, but not volatile without decomposition.

Styrylic Chloride, C^9H^9Cl.—When dry hydrochloric acid gas is passed into crystallised styrylic alcohol, the latter becomes liquid, and separates into two layers; and on heating the product to 100°, washing with dilute soda-ley, and drying with calcic chloride, styrylic chloride is obtained as an oil of light wine-yellow colour, smelling of cinnamon and anise-oils, remaining liquid at −19°, and decomposed by distillation, even in a vacuum.

Heated with cyanide of potassium, either in open vessels or to 100° in sealed tubes, it yields a reddish oil, which quickly decomposes, with formation of a resinous mass, and cannot be purified by distillation.

Styrylic Cinnamate, $C^9H^{16}O^2 = C^9H^7(C^9H^9)O^2$.—Syn. with Cinnylic Cinnamate or Styracin (i. 986).

Styrylic Cyanide, $C^{10}H^9N = C^9H^9.CN$, is produced by heating styrylic iodide with an alcoholic solution of potassic cyanide to 100° in sealed tubes; on opening the tubes, a strong odour of cyanogen becomes perceptible, and an oily layer separates on cooling. Addition of water renders the contents of the tubes milky, and, on further adding common salt, the styrylic cyanide separates as a yellowish oil, easily soluble in ether, sparingly in alcohol, insoluble in water. When heated with potash, it gives off ammonia, and becomes resinised, but does not appear to yield an acid homologous to cinnamic acid.

Styrylic Iodide, C^9H^9I, is produced by the action of iodide of phosphorus on styrylic alcohol. The action takes place without aid of heat; the styrylic alcohol melts, and the mixture, when warmed, separates into two layers, the upper of which consists of styrylic iodide, to be purified like the chloride. It is heavier than water; has an aromatic odour, and burning taste; cannot be distilled, either alone or with water.

Styrylic Oxide, $(C^9H^9)^2O$, is produced by the action of boric anhydride on styrylic alcohol. When the two substances are triturated together, the alcohol first melts, and the mixture solidifies; and on heating it in sealed tubes to 100°, for five or six hours, the formation of the styrylic oxide is completed; the product may be freed from boric acid by means of soda-solution.—Styrylic oxide is a light-yellow viscid oil, having an odour of cinnamon, heavier than water, partially decomposed by distillation.

Styryl-ethylic Oxide, $C^9H^9.C^2H^5.O$, produced by the action of sodic ethylate on styrylic chloride, is a liquid heavier than water, insoluble therein, easily soluble in alcohol and ether, and distilling at a very high temperature.

Styrylic Sulphide, $(C^9H^9)^2S$, obtained by mixing the alcoholic solutions of styrylic chloride and potassic monosulphide, is a yellowish, fetid, non-distillable oil.

STYRYLINE. The name given by Chiozza to a base, C^9H^9N, probably formed by the action of ammonium-sulphide on metastyrol (i. 983).

SUBERAMIC ACID. $C^8H^{15}NO^3 = \left.\begin{matrix} H^2 \\ (C^8H^{12}O^2)'' \\ H \end{matrix}\right\} \begin{matrix} N \\ O \end{matrix}$.—Produced by the dry distillation of ammonium-suberate. It is fusible, soluble in boiling water, and deposited therefrom on cooling. On boiling it with barium-carbonate, and treating the filtrate with silver-nitrate, a gelatinous precipitate is formed, containing 38 per cent. silver, agreeing approximately with the formula $C^8H^{14}AgNO^3$, which requires 38·57 per cent. silver. (Gerhardt, Compt. chim. 1845, p. 178.)*

SUBERAMIDE. $C^8H^{16}N^2O^2 = N^2(C^8H^{12}O^2)^{11}.H^4$.—White crystalline substance, produced by the action of aqueous ammonia on methylic suberate, or by passing ammoniacal gas into an alcoholic solution of ethylic suberate. (Laurent, J. pr. Chem. xxvii. 313.)

SUBERANILIC ACID *Phenyl-suberamic Acid*, $C^{14}H^{19}NO^3 = \left.\begin{matrix} C^6H^5.H \\ (C^8H^{12}O^2)'' \\ H \end{matrix}\right\} \begin{matrix} N \\ O \end{matrix}$. (Laurent and Gerhardt, Ann. Ch. Phys. [3] xxiv. 185.)—Produced, together with suberanilide, by melting suberic acid with an equal volume of dry aniline. When the alcoholic liquid from which suberanilide is precipitated by water, is evaporated till the alcohol is driven off, a brownish oil separates, which solidifies on cooling. This oil is dissolved in boiling ammonia, which leaves a certain quantity of suberanilide, and filtered; from the filtrate hydrochloric acid precipitates colourless suberanilic acid. If during the boiling a slight excess of hydrochloric acid be added, suberanilic acid will separate on cooling, partly crystalline, and partly as a pale-yellowish oil, which afterwards solidifies.

The acid forms microscopic laminæ, irregularly notched, melts at 128°, becoming crystalline on cooling. It is not soluble in cold, and but slightly soluble in hot water. It dissolves readily in ether. The solution in hot water reddens litmus. By dry distillation it yields much charcoal, and a thick oil containing aniline, which partly solidifies on cooling. Fused with potash it yields aniline.

Suberanilate of Ammonium.—The acid dissolves easily in hot ammonia, and the salt is deposited in small granular crystals, whose aqueous solution is not coloured by chloride of lime.

The ammonium-salt precipitates *chloride of barium*; the precipitate dissolves readily in boiling water, and separates on cooling in woolly flakes. With *chloride of calcium* it gives a white precipitate, soluble in hot water; with *lead-salts* a white precipitate, insoluble in water. It precipitates *ferrous salts* yellowish-white, *cupric salts* light-blue, the precipitate being insoluble in water; with *silver-nitrate* a white precipitate, insoluble in water, and turning violet on exposure to light.

SUBERANILIDE. *Phenyl-suberamide.* $C^{20}H^{24}N^2O^2 = \left.\begin{matrix} (C^8H^{12}O^2)'' \\ (C^6H^5)^2 \\ H^2 \end{matrix}\right\} N^2$. (Laurent and Gerhardt, *loc. cit.*)—When equal measures of dry aniline and fused suberic acid are melted together, water is produced. The mixture is kept melted for ten minutes near the boiling heat; and an equal bulk of alcohol is then added, which immediately dissolves the mixture. After a few minutes the solution solidifies to a mass of crystals, which are dissolved in more boiling alcohol, and the solution is left to stand, whereupon most of the suberanilide crystallises out. The rest is precipitated by water, suberanilic acid remaining in solution.

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* In his *Traité de Chimie organique* (ii. 735), published in 1854, Gerhardt states, however, that suberamic acid has not yet been obtained.

Suberanilide crystallises from alcohol in pearly laminæ. It melts at 183°, and crystallises on cooling. It is but slightly soluble in cold alcohol, but dissolves readily in boiling alcohol and in ether.

When subjected to dry distillation, it leaves a small quantity of charcoal, and yields an oil, which solidifies on cooling, and crystallises from a hot alcoholic solution in pearly laminæ, which however present a different appearance under the microscope, and seem to be somewhat rounded. Gently heated with hydrate of potassium, it immediately gives off aniline. It is not attacked by ammonia, or by boiling solution of potash.

SUBERIC ACID. $C^8H^{14}O^4 = \left.\begin{matrix}(C^8H^{12}O^2)''\\ H^2\end{matrix}\right\}O^2$.—*Korksäure.* (Brugnatelli, Crell. Ann. 1787, i. 145.—Bouillon Lagrange, Ann. Chim. xxiii. 2; J. Pharm. viii. 107.—Chevreul, Ann. Chim. lxii. 323; xcvi. 182.—Brandes, Schw. J. xxxii. 393; xxxiii. 83; xxxvi. 263; Ann. Ch. Pharm. ix. 295.—Bussy, J. Pharm. viii. 107; xix. 425.—Boussingault, J. pr. Chem. vii. 211.—Harff, N. Br. Arch. v. 303.—Laurent, Ann. Ch. Phys. [2], lxvi. 157.—Bromeis, Ann. Ch. Pharm. xxxv. 89.—Tilley, *ibid.* xxxix. 166.—Sacc, *ibid.* li. 222.—Wirtz, *ibid.* civ. 261.—Arppe, *Oxidation of Fats by Nitric Acid*, Ann. Ch. Pharm. cxv. 143; cxx. 288: Jahresb. 1860, p. 246; 1861, p. 357; 1864, p. 377.—Gm. xiii. 204.)

This acid, belonging to the oxalic series, $C^nH^{2n-2}O^4$ (i. 52), was first obtained by the action of nitric acid upon cork (Brugnatelli): hence its name (from the Latin *suber*). It is also produced, together with several other acids of the same series, by the oxidising action of nitric acid on various fatty bodies—*e.g.* oleic acid (Laurent), stearic acid (Bromeis), castor-oil (Tilley), linseed-oil (Sacc), cocoanut-oil (Wirtz); lastly, it is produced by the action of nitric acid on suberone (p. 450).

It is most easily prepared by treating commercial stearic or oleic acid, or castor-oil, with nitric acid, in the manner described under LEPARGYLIC ACID (iii. 571) and PIMELIC ACID (iv. 646). The resulting acid solution, when duly concentrated, yields a white granular mass, which, when freed from oxalic acid by washing with cold and recrystallisation from warm water, and from other more soluble acids by melting the crystals, pulverising the fused mass, and treating the powder with water, yields a mixture of azelaic (lepargylic) and suberic acids; and on treating this residue with cold ether, the azelaic acid is dissolved, while the suberic acid remains behind. Further purification may be effected by repeated treatment with water and ether successively.

Pure suberic acid crystallises, according to Arppe, in needles an inch long, or in tabular crystals (six-sided tables of 120°, apparently belonging to the hexagonal system). It melts at 140°, solidifies in transparent sharp needles, and sublimes between 150° and 160°, with partial decomposition, in slender needles half an inch long. It dissolves sparingly in cold, easily in boiling *water*, more easily in *alcohol* than in water, sparingly in *ether;* sparingly in cold, easily in warm *oil of turpentine*, and mixes with *fixed oils*.

Suberic acid, when heated in a test-tube, gives off suffocating vapours, condensing into drops which become solid and crystalline. It is decomposed by prolonged boiling with *nitric acid*, forming an oily acid, which has the odour of butyric acid (Sacc). Distilled with 4 pts. *manganic peroxide*, 1 pt. oil of vitriol, and 1 pt. water, it yields an acid distillate, smelling of formic acid (Brandes). Distilled with excess of *lime*, it yields suberone (p. 450), together with other products. Distilled with excess of *baryta*, it yields at 80° a liquid distillate, from which by rectification a hydrocarbon is obtained, having the composition C^6H^{14}, and boiling at 76°; $C^8H^{14}O^4 = 2CO^2 + C^6H^{14}$ (Riche, Ann. Ch. Pharm. cxiii. 105). According to R. S. Dale (Chem. Soc. J. [2] ii. 258), the acid distilled with anhydrous or hydrated baryta yields, at a temperature near redness, a yellowish oil, from which, by treatment with a mixture of nitric and sulphuric acids, and subsequent rectification, a hydrocarbon, C^6H^{14}, is obtained, agreeing in properties with hexylic hydride obtained from coal-tar, excepting that the somewhat lower specific gravity (0·6617 at 17·5°) brings it nearer to the β-hexylic hydride discovered by Wanklyn and Erlenmeyer (iii. 153).

Suberic acid fused with *aniline* yields suberanilide and suberanilic acid (p. 448).

Suberates.—Suberic acid is dibasic, the formula of its normal salts being $C^8H^{12}M^2O^4$ or $C^8H^{12}M''O^4$. The suberates of the alkali-metals, earth-metals, zinc, and manganese are more or less soluble in water; and from their solutions, the suberic acid is precipitated by stronger acids as a white powder. They are decomposed by distillation, yielding a white sublimate of the acid.

The aqueous solution of suberic acid does not precipitate any metallic salt except neutral acetate of lead. When saturated with ammonia, it precipitates the solutions of barium-, calcium-, and strontium-chlorides only on addition of alcohol, but forms an immediate white precipitate in solutions of the neutral salts of silver, mercury, zinc, and tin—bluish-green with cupric sulphate, red-brown with ferric sulphate.

The composition and physical characters of the suberates, as determined by Arppe, are as follows:

Neutral suberate of sodium	$2C^8H^{12}Na^2O^4.H^2O$	warty or dendritic aggregates.
Acid „	$C^8H^{13}NaO^4$	tufts of needles.
Suberate of barium	$C^8H^{12}Ba''O^4$	crystalline precipitates.
„ strontium	$C^8H^{12}Sr''O^4$	
„ calcium	$2C^8H^{12}Ca''O^4.H^2O$	
„ magnesium	$C^8H^{12}Mg''O^4.3H^2O$	warty crystalline aggregates.
„ aluminium	. . . .	white amorphous powder.
„ zinc	$C^8H^{12}Zn''O^4$	fine granular precipitate.
„ manganese	$C^8H^{12}Mn''O^4.3H^2O$	light-red crystalline spangles.
„ „	$C^8H^{12}Mn''O^4$	produced on boiling.
„ copper	$C^8H^{12}Ca''O^4.H^2O$	green precipitate.
„ silver	$C^8H^{12}Ag^2O^4$	white precipitate.
„ lead	$C^8H^{12}Pb''O^4$	white precipitate.
„ „ (basic)	$C^8H^{12}Pb''O^4.2Pb''O$	produced on boiling with ammonia.

SUBERIC ETHERS. *Ethylic Suberate*, $C^{12}H^{22}O^4 = \left.\begin{matrix}(C^8H^{12}O^2)''\\(C^2H^5)^2\end{matrix}\right\}O^2$, is obtained by heating suberic acid with alcohol and sulphuric or hydrochloric acid, or by passing hydrochloric acid gas into an alcoholic solution of suberic acid. It is a limpid liquid, having a faint odour and nauseous taste. Specific gravity = 1·003 at 15°. Boils without decomposition at 230° (Bromeis), at 260° (Laurent). It mixes in all proportions with alcohol and ether. It is scarcely attacked by aqueous potash, but alcoholic potash quickly decomposes it. With alcoholic ammonia it yields suberamide (p. 448). By chlorine it is slowly converted into chlorethylic suberate, $C^{12}H^{20}Cl^2O^4$. (Laurent.)

Methylic Suberate, $C^{10}H^{18}O^4 = \left.\begin{matrix}(C^8H^{12}O^2)''\\(CH^3)^2\end{matrix}\right\}O^2$.—Prepared like the ethyl-compound which it resembles. Specific gravity = 1·014 at 18°. Forms suberamide with ammonia. (Laurent.)

SUBERIN. Cellulose from cork.

SUBERONE. *Hydride of Suberyl.*—When suberic acid is distilled with excess of lime, a distillate is obtained, which yields by rectification an aromatic liquid boiling at 176°, and probably consisting of suberone, the ketone of suberic acid, $C^{14}H^{24}O^2 = (C^8H^{12}O^2)''(C^6H^{12})''$—its formation taking place thus:

$$2C^8H^{14}O^4 = 2CO^2 + 2H^2O + C^{14}H^{24}O^2.$$

Its composition has not, however, been ascertained with certainty, and, moreover, it differs from ketones in general in being converted into suberic acid by the action of nitric acid. (Boussingault, Ann. Ch. Pharm. xix. 308.—Tilley, *ibid.* xxxix. 167.)

SUBERYL. $C^8H^{12}O^2$.—The diatomic radicle of suberic acid, &c. Boussingault applied the same term to the radicle $C^8H^{12}O$, which he supposed to exist in the so-called suberone, that compound having, according to his analysis, the composition $C^8H^{14}O = (C^8H^{12}O)''H^2$.

SUBLIMATE. A body obtained in the solid state by the cooling of its vapour—*e. g.* sulphur, iodine, sal-ammoniac, mercuric chloride (corrosive sublimate, &c.)

SUBRUBRIN. The name applied by O'Shaughnessy (Ann. Ch. Pharm. xv. 265) to a faintly reddish body, which he obtained from blood-serum by mixing it with alcohol, filtering, and heating the turbid filtrate; but its separate identity is not established by any satisfactory evidence.

SUBSTITUTION. Under the head of EQUIVALENTS, frequent allusion has been made to the substitution of one element for another. Substitution is, in fact, the great agent of chemical change. The instances in which compounds are formed by direct union of their elements, ultimate or proximate, or decomposed by direct separation of those elements, are comparatively rare; and even these may often be regarded as particular cases of substitution (see CHEMICAL AFFINITY, i. 857): thus the formation of hydrochloric acid, when chlorine and hydrogen come in contact, may be supposed to take place by an interchange of these elements between a molecule of chlorine and a molecule of hydrogen, each consisting of two atoms:

$$\overset{-}{Cl}\overset{+}{Cl} + \overset{-}{H}\overset{+}{H} = HCl + HCl.$$

The following are the most important cases of substitution:—

1. Of *Chlorous* or *Acid Radicles* for *Hydrogen.*—Chlorine and bromine may, in many instances, be introduced into hydrogen-compounds (chiefly organic) by direct substitution, 1 atom of hydrogen being removed and entering into combination with 1 at. chlorine or bromine, while another atom of the haloïd element takes the place of the hydrogen removed. Thus, when chlorine acts upon marsh-gas (methylic hydride), the products are hydrochloric acid and methylic chloride:

$$CH^4 + Cl^2 = HCl + CH^3Cl;$$

and by the continued action of the chlorine, the latter compound may be converted, successively, into CH^2Cl^2 and $CHCl^3$, the last being the compound usually called chloroform. In like manner, acetic and treated with chlorine in sunshine, in different proportions, yields mono- and tri-chloracetic acid:

$$C^2H^4O^2 + Cl^2 = HCl + C^2H^3ClO^2.$$
$$C^2H^4O^2 + 3Cl^2 = 3HCl + C^2HCl^3O^2.$$

Iodine does not act on hydrogen-compounds so easily as chlorine and bromine; but when it is presented in the form of chloride or bromide of iodine, an action takes place exactly similar to that just described, an atom of hydrogen being removed by the chlorine or bromine, and its place supplied by an atom of iodine: *e.g.*—

$$C^5H^4O^3 + ClI = HCl + C^5H^3IO^3.$$

Pyromeconic acid. Iodopyromeconic acid

In some cases an organic compound first unites directly with 2 at. chlorine or bromine, and the product, when treated with alcoholic potash, splits up into hydrochloric or hydrobromic acid (which is removed by the alkali), and a chloro- or bromo-substitution-product: thus ethylene takes up 2 at. chlorine, forming the compound, $C^2H^4Cl^2$ (Dutch liquid), which is resolved by alcoholic potash into HCl and monochlorethylene, C^2H^3Cl. This in like manner takes up 2 at. Cl, forming $C^2H^3Cl^3$, resolvable into HCl and dichlorethylene, $C^2H^2Cl^2$; and by a repetition of these processes, the compounds C^2HCl^3 and C^2Cl^4 are obtained (ii. 573). The chloro- and bromo-naphthalenes are prepared from naphthalene by a similar series of processes (iv. 10).

Oxygen may be substituted for hydrogen (O'' for H^2 or HO for H), by exposing organic compounds to the action of oxidising agents, a familiar example of which is the conversion of alcohol, C^2H^6O, into acetic acid.

Nitro-substitution, or the substitution of nitryl, NO^2, for hydrogen, is effected by subjecting organic compounds to the action of fuming nitric acid, or of a mixture of strong nitric and sulphuric acids, as in the conversion of cellulose into pyroxylin.

Allied to this is the substitution of nitrogen for hydrogen (N for H^3), by the action of nitrous acid on certain organic compounds, as in the formation of the diazo-compounds discovered by Griess (iv. 292, 460): thus aniline, C^6H^7N, is converted by the action of nitrous acid into diazobenzene, $C^6H^4N^2$:

$$C^6H^7N + NHO^2 = C^6H^4N^2 + 2H^2O.$$

2. Of *Hydrogen* and other *Basylous Radicles* for *Chlorous Radicles.*—This reaction, sometimes called inverse substitution, is effected by the action of reducing agents. Chlorinated acids are easily reduced to the primary acids from which they are derived by the action of sodium-amalgam; the first transformation of the kind that was effected was that of trichloracetic into acetic acid. The conversion of nitro-compounds into amidogen-compounds (substitution of NH^2 for NO^2), by the action of sulphydric acid or ferrous acetate, also comes under this head. The well-known preparation of amidobenzene (aniline), $C^6H^5(NH^2)$, from nitrobenzene, $C^6H^5(NO^2)$, may be taken as an example.

An important class of reactions belonging to this head is the substitution of alcohol-radicles for chlorine, oxygen, &c. by the action of the zinc-compounds of the alcohol-radicles: *e.g.*, the preparation of triethylphosphine, $P(C^2H^5)^3$, by the action of zinc-ethyl on trichloride of phosphorus:

$$3Zn''(C^2H^5)^2 + 2PCl^3 = 3ZnCl^2 + 2P(C^2H^5)^3.$$

Another example of this kind of action is the formation of diethoxalic acid and its homologues, by the action of zinc-ethyl, &c. on the oxalic ethers (iv. 272).

3. Of *Basylous* or of *Chlorous Radicles, one for the other.*—To this head belong the innumerable instances of the mutual decomposition of salts, and of double decomposition in general (CHEMICAL AFFINITY, i. 855); also, on the one hand, the precipitation of metals from their solutions, one by the other (as of copper by iron, lead by zinc, &c.), the decomposition of acids by metals, with evolution of hydrogen; and, on the other, the decomposition of bromides and iodides by chlorine, and of iodides by bromine—the

conversion of sulphides into oxides by direct oxidation, &c. Many of these reactions appear to consist in a simple substitution of one element for another, which is eliminated without entering into any new combination. But, on closer examination, they are found to be, at least in some cases, analogous to the chlorine-substitutions already considered. In the oxidation of sulphides, for example, a considerable portion, if not all, of the sulphur eliminated is oxidised to sulphurous anhydride; in the decomposition of bromides and iodides by chlorine, the latter, if in excess, unites with the eliminated bromine or iodine; and even in the precipitation of one metal by another, alloys are frequently formed, as in the precipitation of silver by mercury.

An important class of reactions belonging to this place is the substitution of alcohol-radicles for hydrogen and metals, as in the several processes of etherification by the action of acids on alcohols, of alcoholic chlorides, iodides, &c., on alcohols, and on the silver-salts of acids (see Ethers, ii. 511, 512). The formation of amines, or, in other words, the replacement of the hydrogen in ammonia by alcohol-radicles, may be effected directly, as when an alcoholic iodide is heated with ammonia in sealed tubes (ii. 554, iii. 994); or by indirect methods, as by distilling cyanic or cyanuric ethers with caustic alkali.

Most of the methods of producing organo-metallic bodies, consist in acting on alloys of potassium or sodium with the alcoholic iodides, bromides, &c.: *e.g.*—

$$\underset{\substack{\text{Methylic}\\\text{iodide.}}}{2(CH^3)I} + Na^2Hg'' = \underset{\substack{\text{Mercuric}\\\text{methide.}}}{(CH^3)^2Hg''} + 2NaI;$$

or by acting on a metallic chloride with the zinc-compound of an alcohol-radicle: *e.g.*—

$$Zn''(C^2H^5)^2 + Hg''Cl^2 = Hg''(C^2H^5)^2 + Zn''Cl^2.$$

Substitution-derivatives often exhibit a marked resemblance to their primitives in physical and chemical characters. That this should be the case in bodies formed from one another by the interchange of similar elements or radicles—such as hydrogen and the metals on the one hand, or chlorine, bromine, and iodine on the other—is nothing more than might have been anticipated on any view of the constitution of chemical compounds; but that a radicle of decidedly acid or chlorous character, like chlorine, bromine, or iodine, should be capable of replacing hydrogen atom for atom, and discharging functions similar to that of the hydrogen in the primary compound, is the doctrine of a comparatively recent date, and is, in fact, diametrically opposed to the older views of the constitution of compounds, founded on the electrical relations of their elements. The resemblance of such derivatives to their primitives is, however, strikingly exhibited in numerous instances. Take, for example, acetic and trichloracetic acid. These two acids are both crystallisable, deliquescent, soluble in water and alcohol, have the same capacity for saturation, yield analogous salts and ethers, &c. Dilute trichloracetic acid treated with amalgam of sodium, is reconverted into normal acetic acid; and the two acids, when heated with caustic alkali, are decomposed according to similar equations, yielding the two analogous bodies, marsh-gas and chloroform, thus:

Acetic acid . . . $C^2H^4O^2 = CO^2 + CH^4$ Marsh-gas.
Trichloracetic acid . $C^2HCl^3O^2 = CO^2 + CHCl^3$ Chloroform.

Similar resemblances may be traced between isatin and its derivatives (iii. 406). Thus isatin and chlorisatin are both of an orange-red colour, are isomorphous, partly volatile, slightly soluble in water, more soluble in alcohol and ether; form yellow solutions; and react with hydrate of potassium, by exchanging an atom of hydrogen for one of potassium, to form analogous salts, each of which speedily absorbs an atom of water into its constitution, to form the isatinate and chlorisatinate of potassium respectively. Moreover the two bodies, when acted upon by sulphydrate of ammonium, ammonia, and alkaline bisulphites, yield hosts of analogous compounds, and undergo hosts of analogous reactions. Isatin, chlorisatin, and dichlorisatin treated with hydrate of potassium, yield respectively the bodies, aniline, C^6H^7N, chloraniline, C^6H^6ClN, dichloraniline, $C^6H^5Cl^2N$, each of which, despite the constituent chlorine, has alkaline characters analogous to those of ammonia, and can unite directly with acids to form salts.

The chlorinated derivatives of the natural alkaloïds also resemble the primary alkaloïds in many important respects. Thus dichlorocinchonine, $C^{20}H^{22}Cl^2N^2O$, formed from cinchonine by the direct action of chlorine, resembles the normal base, not only in alkalinity, solubility, crystalline form, &c., but likewise in turning the plane of polarisation of a luminous ray to the left. Chlorostrychnine also, $C^{21}H^{21}ClN^2O^2$, obtained from strychnine or its salts by direct substitution of chlorine, produces poisonous effects, undistinguishable from those of the natural alkaloïd.

From the observation of such resemblances, Dumas and Laurent were led to conclude that elements, even of opposite chemical character, may in many instances replace one another, with but little alteration in the character of the products, and that the properties of a compound are determined by the arrangement and relative position of its atoms more than by their individual character. That this is the case to a considerable extent, is evident from the instances just cited; nevertheless, the question is altogether one of degree. Substitution is always attended with some alteration of properties in the compound, and the alteration goes on increasing with the amount of the substitution. Thus in volatile compounds, such as ethylene, C^2H^4, and its chlorinated derivatives, C^2HCl^3, $C^2H^2Cl^2$, C^2HCl^3, and C^2Cl^4, the vapour-density increases, and the boiling-point rises with each successive replacement of H by Cl. Again, in the chloranilines (iv. 438), the first substitution-product, C^6H^6ClN, is somewhat less basic than aniline itself; while dichloraniline, $C^6H^5Cl^2N$, is still less basic, and in trichloraniline, $C^6H^4Cl^3N$, the basic character has altogether disappeared.

The substitution of alcohol-radicles, such as ethyl and methyl, for the hydrogen of ammonia, gives rise to amines, which are basic like ammonia itself; but in the amides derived from ammonia by substitution of acid-radicles (benzoyl, acetyl, &c.) for hydrogen, the basic character gives place for the most part to an acid character, the amide, if it still retains replaceable hydrogen, exhibiting a tendency to exchange it for a metal. (For the further consideration of this subject, see TYPES.)

SUCCINAMIC ACID, SUCCINAMIDE, SUCCINANIL, SUCCINANILIC ACID, SUCCINANILIDE. See SUCCINIC ACID, AMIDES OF.

SUCCINASPHALT. A resinous substance resembling amber, and apparently related to retinite, obtained from the granular clay iron-ore of Bergen in Bavaria. (Wagner, *Handw. d. Chem.*, viii. 414.)

SUCCINEUPIONE. A name applied by Elsner to a very light oil, obtained by rectifying oil of amber with sulphuric acid.

SUCCINIC ACID. $C^4H^6O^4 = \left.\begin{matrix}(C^4H^4O^2)''\\H^2\end{matrix}\right\}O^2$. *Volatile Salt of Amber. Bernsteinsäure.* (Berzelius, Ann. Chim. xciv. 187.—Lecanu and Serbat, J. Pharm. viii. 541; ix. 89.—Liebig and Wöhler, Pogg. Ann. xviii. 162.—D'Arcet, *ibid.* xxxvi. 80.—Döpping, Ann. Ch. Pharm. xlvii. 253.—Fehling, *ibid.* xlix. 154.—Piria, *ibid.* lxviii. 343.—Dessaignes, *ibid.* lxx. 102.—Pasteur, *ibid.* cv. 264.—Maxwell Simpson, *ibid.* cxviii. 373.—Gm. x. 108.—Gerh., ii. 454.—Kekulé, *Lehrb.* ii. 23.)

This acid, the third of the series of dibasic acids, $C^nH^{2n-2}O^4$, homologous with oxalic acid, was mentioned as *volatile salt of amber* by Agricola, as early as 1657; its acid nature was recognised by Barchhusen, Bouldüc, and Boerhaave; but the first exact investigations of it were made by Berzelius and by D'Arcet.

Succinic acid occurs ready-formed in amber, and in certain lignites, as in those of Muskau, Naumberg, and Altenburg. It has also been found in the turpentine of several species of pine, and in certain plants—viz., in the herb of *Lactuca virosa, Artemisia Absinthium*, &c. According to Walz (N. Jahrb. f. Pharm. xv. 22), the chelidoninic acid found by Zwenger in the mother-liquor of the preparation of chelidonic acid from *Chelidonium majus* (i. 850), is nothing but succinic acid. It is also occasionally found in the animal organism—*e.g.*, in the thymoïd gland of the calf, the spleen of the ox, (Gorup-Besanez), and in certain pathological exudations (Heintz). According to G. Meissner and F. Jolly (Jahresb. 1865, p. 675), it occurs in the urine of dogs fed on flesh and fat, and in that of rabbits fed on carrots.

Formation.—1. Succinic acid is a frequent product of the oxidation of organic substances, especially of fats. All the fatty acids of the series, $C^nH^{2n}O^2$, from butyric acid upwards, when oxidised with nitric acid, yield succinic acid, together with other acids of the same series (p. 449). Its formation from butyric acid is represented by the equation:

$$C^4H^8O^2 + O^3 = H^2O + C^4H^6O^4.$$

According to Pasteur (Bull. Soc. Chim. 1852, p. 52), it is always formed during the conversion of alcohol into acetic acid under the influence of *Mycoderma aceti*, especially when the plant grows on the surface of the alcoholic liquid containing phosphates.

2. By the action of reducing agents on malic acid or its isomer, fumaric acid, which contains 2 at. hydrogen less, or on maleic and tartaric acids, which contain respectively 1 and 2 at. oxygen more than succinic acid.

a. By the action of sodium-amalgam on maleic or fumaric acid:

$$\underset{\substack{\text{Maleic}\\\text{acid.}}}{C^4H^4O^4} + Na^2Hg = Hg + \underset{\substack{\text{Succinate}\\\text{of sodium.}}}{C^4H^4Na^2O^4}.$$

Chloromaleic acid, $C^4H^3ClO^4$ (iii. 788), is also converted into succinic acid by the action of sodium-amalgam:

β. From malic or tartaric acid by the action of hydriodic acid (**R. Schmitt**, Ann. Ch. Pharm. cxiv. 106), or of iodide of phosphorus (**Dessaignes**, *ibid.* cxv. 120; cxvii. 134):

$$\underset{\text{Malic acid.}}{C^4H^6O^5} + 2HI = H^2O + I^2 + \underset{\text{Succinic acid.}}{C^4H^6O^4}.$$

$$\underset{\text{Tartaric acid.}}{C^4H^6O^6} + 4HI = 2H^2O + 2I^2 + \underset{\text{Succinic acid.}}{C^4H^6O^4}.$$

3. In many processes of fermentation, *e.g.*, of asparagin (**Piria**), malic, maleic, fumaric, and aconitic acids (**Dessaignes**), and of sugar, whence it is constantly present, to a small amount, in wine and beer (**Pasteur**). Its formation from malic, maleic, or fumaric acid is probably a simple process of reduction. Its formation from asparagin may be represented by the equation:

$$C^4H^8N^2O^3 + 3H^2O - O^2 = 2NH^3 + C^4H^6O^4.$$

4. By heating cyanide of ethylene to 100° with alcoholic potash (**Maxwell Simpson**, Ann. Ch. Pharm. cxviii. 373):

$$C^2H^4(CN)^2 + 2KHO + 2H^2O = 2NH^3 + C^4H^4K^2O^4.$$

This reaction is precisely analogous to that by which the monobasic acids of the series, $C^nH^{2n}O^2$, are formed from the cyanides of monatomic alcohols (ii. 202). Cyanide of ethylene is also converted into succinic acid by heating with nitric or hydrochloric acid. (**Simpson**, *ibid.* 153.)

Preparation: 1. *From Amber.*—This substance, subjected to dry distillation, yields succinic acid and a volatile oil, together with water and a small quantity of a resinous substance called *Colophonium succini*. On heating the watery distillate to the boiling-point, and filtering hot, a large quantity of oil remains behind; and the solution, on cooling, yields crystallised succinic acid, contaminated however with a considerable quantity of empyreumatic oil, from which it may be freed for the most part, but not perfectly, by repeated crystallisation. Complete purification is, however, easily effected by treating the crude succinic acid with nitric acid.

2. *By fermentation of Malic Acid.*—This is the most advantageous mode of preparing succinic acid, the crude malate of calcium, obtained by neutralising the juice of mountain-ash berries with chalk or slaked lime, being generally used for the purpose. A mixture of 1 pt. of this salt with 6 pts. water and ½ pt. yeast, or 3 pts. water and $\frac{1}{12}$ pt. decayed cheese, is placed in an earthen jar, and left for four to six days at a temperature of 30° to 40°, till the evolution of gas has ceased. The granular precipitate is then collected upon linen, washed several times with water, and mixed with dilute sulphuric acid till it no longer effervesces (from admixed calcic carbonate); another equal quantity of sulphuric acid is then added; the mixture boiled for awhile, till the calcium-salt is no longer granular; the liquid strained through linen; the precipitate on the filter thoroughly washed; the whole of the liquid evaporated till a crystalline crust forms on the surface; oil of vitriol then added in small quantities, as long as gypsum is thereby precipitated; the liquid strained off (after dilution with water, if the gypsum forms a paste); the precipitate washed; and the whole of the liquid again evaporated: it then yields, on cooling, brownish crystals of succinic acid, still contaminated with gypsum. These crystals are purified by recrystallisation from water, sometimes with addition of animal charcoal, and ultimately freed from gypsum by solution in alcohol or by sublimation. By this process, 12 pts. of calcic malate yield from 3·75 to 4 pts. of pure crystallised succinic acid: the mother-liquors do not retain a trace of malic acid. Three pounds of calcic malate thus treated yield about one pound of pure succinic acid. (**Liebig.**)

The formation of succinic acid in this process is accompanied by that of acetic acid and carbonic anhydride: hence the reaction is commonly represented by the equation:

$$\underset{\text{Malic acid.}}{3C^4H^6O^5} = \underset{\text{Succinic acid.}}{2C^4H^6O^4} + \underset{\text{Acetic acid.}}{C^2H^4O^2} + 2CO^2 + H^2O.$$

Probably two reactions go on simultaneously, one part of the malic acid being converted by fermentation into acetic acid, and this fermentation causing the reduction of another portion into succinic acid (**Kekulé**). See MALATE OF CALCIUM (iii. 702).

Properties.—Succinic acid crystallises in prisms belonging to the monoclinic system, generally in rhombic or hexagonal plates, the face ∞P∞ replacing the acute edge of the vertical prism ∞P. The crystals are permanent in the air, have an acid taste, but no smell. Succinic acid is much more soluble in hot than in cold water—viz., in 5 pts. water at 16°, and 2·2 pts. at 100° (**Lecanu** and **Serbat**). It is less soluble in alcohol, and nearly insoluble in ether. It melts at 180°, but begins to emit suffocating vapours even below its melting-point. It boils at 235°, being resolved into water and succinic anhydride.

Decompositions.—1. Succinic acid offers great resistance to the action of oxidising agents, not being affected by nitric acid, chromic acid, chlorine-water, or a mixture of hydrochloric acid and potassic chlorate. When evaporated to dryness with *manganic peroxide* and *sulphuric acid*, it yields acetic acid (Trommsdorff).—2. An aqueous solution of sodic succinate is decomposed by the *electric current*, giving off at the positive pole a mixture of carbonic anhydride and methylic oxide (Kolbe, Ann. Ch. Pharm. cxiii. 244):

$$C^4H^6O^4 + H^2O = (CH^3)^2O + 2CO^2 + H^2.$$

3. When fused with *potassic hydrate*, it yields carbonate and oxalate, together with a gaseous hydrocarbon (Liebig and Wöhler).—4. It is not attacked by strong sulphuric acid (H^2SO^4) even when heated, but *sulphuric anhydride* converts it into succinosulphuric acid.—5. Heated with *bromine*, it forms substitution-products.— 6. By *dehydrating substances*, such as *phosphoric anhydride* and *phosphoric pentachloride*, it is converted into succinic anhydride; in the latter case with formation of hydrochloric acid and phosphoric oxychloride.

Succinates. Succinic acid is dibasic, the general formula of its salts being as follows:

Neutral Succinates	$C^4H^4M^2O^4$ and $C^4H^4M''O^4$
Acid "	$C^4H^5MO^4$ and $C^8H^{10}M''O^8$. $= C^4H^4M''O^4.C^4H^6O^4$.

There are also a few double succinates, several basic lead-salts, and a hyperacid potassium-salt.

Most succinates resist a temperature of 200° without decomposition. When distilled with acid phosphate or sulphate of sodium, they yield a sublimate of succinic anhydride.

The succinates of the alkali-metals and of magnesium are easily soluble in water; those of the alkaline earth-metals, and most other diatomic metals, are sparingly soluble; those of sesqui-atomic metals are insoluble.

Succinic acid and soluble succinates form, with *ferric salts*, a red-brown precipitate resembling that formed by benzoic acid, but much more compact: hence succinate of ammonium is a more convenient reagent for the precipitation of ferric salts than the benzoate. With *acetate of lead*, succinic acid forms a precipitate of succinate of lead, soluble in excess of either reagent. With *chloride of barium*, the acid by itself gives no precipitate; but on addition of ammonia and alcohol, a white precipitate is formed: benzoic acid does not exhibit this reaction. Succinic acid is further distinguished from benzoic acid by not being precipitated from its soluble salts by a mineral acid.

Succinate of Ammonium.—The *neutral salt*, $C^4H^4(NH^4)^2O^4$, is obtained by supersaturating succinic acid with ammonia, and leaving the solution to evaporate over quicklime; it is also formed, according to Piria, in the putrefaction of asparagin. It crystallises in hexagonal prisms, very soluble in water and in alcohol. Gives off ammonia when exposed to the air, and is resolved by heat into ammonia, water, and succinamide. Specific gravity = 1·367 (Bödeker, Jahresb, 1860, p. 17).—The *acid salt*, $C^4H^5(NH^4)O^4$, is produced when the solution of the preceding salt is evaporated by heat. It crystallises easily, is very soluble in water and alcohol, has an acid reaction, and is decomposed by heat, like the neutral salt. The crystals are triclinic, usually exhibiting the combination: $oP \,.\, 'P_,\infty \,.\, {}_,P'\infty \,.\, \infty\bar{P}\infty \,.\, \infty\breve{P}\infty \,.\, \infty P_,'$. Angle $oP : \infty P\infty = 91° 53'$; $oP : \infty\breve{P}\infty = 93° 25'$; $oP : \infty_,P' = 91° 45'$; $oP : 'P_,\infty = 151° 57'$; $oP : {}_,\bar{P}'\infty = 151° 7'$; $\infty\bar{P}\infty : \infty\breve{P} = 100° 15'$; $\infty\breve{P}\infty : '\bar{P}_,\infty = 119° 53'$; $\infty\breve{P}\infty : \bar{P}_,\infty = 117°$; $\infty\breve{P}\infty : \infty P'_, = 135° 46'$. (Brooke, Ann. Phil. xxii. 286.)

Succinate of Barium, $C^4H^4Ba''O^4$ (at 200°).—White crystalline precipitate, slightly soluble in water, moderately soluble in dilute nitric, hydrochloric, and acetic acid, insoluble in ammonia and in alcohol. With chloride of acetyl it yields a mixture of acetic and succinic anhydrides. (Heintz, Jahresb. 1859, p. 279.)

Succinate of Cadmium crystallises in concentric groups of prisms, very soluble in water. According to John, it appears to be resolved by alcohol into two other salts.

Succinates of Calcium.—The *neutral salt* is gradually deposited, on mixing cold concentrated solutions of calcic chloride and sodic succinate, in small needles, containing $C^4H^4Ca''O^4.3H^2O$. If the solutions are mixed hot, a crystalline precipitate is immediately formed, composed of $C^4H^4Ca''O^4.H^2O$. Both precipitates are sparingly soluble in water and acetic acid, insoluble in alcohol. When heated, it gives off a volatile oil, called succinone, still containing oxygen, but having a composition not yet ascertained with certainty (D'Arcet).—The *acid salt*, $C^8H^{10}Ca''O^8$, or $C^4H^4Ca''O^4.C^4H^6O^4$, obtained by treating the neutral salt with excess of acid, is likewise crystallisable, and slightly soluble in water. Alcohol renders the crystals opaque, and converts them into the neutral salt. They are also decomposed by heating to 150°.

Chromous Succinate, $C^4H^4Cr''O^4.H^2O$, is a scarlet precipitate, formed on adding succinate of sodium to chromous chloride.—*Chromic succinate* is not known.

Succinate of Cobalt.—Peach-blossom-coloured, slightly soluble precipitate. According to Handl (Wien. Akad. Ber. xxxii. 254), it forms monoclinic prismatic crystals: ∞P . ∞P*n* . [∞P∞] . oP. Angle ∞P : ∞P (clinod.) = 113°36′, ∞P*n* : ∞P*n* (clinod.) = 136° 38′ ; oP : ∞P = 115°, nearly.

Succinate of Copper, $C^4H^4Cu''O^4$ (at 200°), is obtained on adding recently precipitated cupric carbonate to a boiling aqueous solution of succinic acid, as a bluish-green crystalline powder, slightly soluble in water and succinic acid, less soluble in acetic acid, insoluble in alcohol and ether.

Succinates of Iron.—α. *Ferric salts.* Alkaline succinates form with ferric salts a red-brown or cinnamon-coloured precipitate, consisting of a basic ferric succinate. The addition of sodic acetate before precipitation renders the precipitate more compact. It dissolves in acetic, succinic, and mineral acids. Ammonia appears to convert it into a still more basic salt.—β. *Ferrous succinate* is a greyish-green precipitate, which oxidises in the air, is slightly soluble in water, easily soluble in succinic acid, partially soluble also in ammonia and ammoniacal salts.

Succinates of Lead.—The *neutral salt*, $C^4H^4Pb''O^4$ (at 100°), is obtained by precipitating neutral acetate of lead with neutral sodic succinate, or a hot solution of succinic acid with basic acetate of lead. It is a white powder, which becomes crystalline if precipitated from hot solutions. It is slightly soluble in water, easily soluble in dilute nitric acid and in potash. Specific gravity = 3·800 (Bödeker).—A *basic salt*, $2C^4H^4Pb''O^4.Pb''O$, is obtained on mixing succinate of sodium with basic acetate of lead, as a glutinous precipitate, which sticks to the sides of the vessel while warm, and becomes brittle on cooling. Another basic salt, $C^4H^4Pb''O^4.2Pb''O$ (at 200°), is produced by treating the neutral salt with excess of ammonia. It is a white powder, insoluble in water, easily soluble in potash, and in dilute nitric acid.

Succinates of Magnesium.—The *neutral salt*, $C^4H^4Mg''O^4.6H^2O$, forms prismatic crystals, which give off all their water at 130°. It is very soluble in water, insoluble in alcohol. The aqueous solution appears to yield, by concentration, crystals containing a smaller proportion of water (Fehling).—A *basic salt*, $2C^4H^4Mg''O^4.4Mg''O.H^2O$ (at 100°?), is obtained as a white pulverulent precipitate, on adding ammonia to a solution of the neutral salt.—*Magnesio-potassic succinate*, $C^8H^8Mg''K^2O^8.5H^2O$, crystallises in fine double six-sided pyramids, very soluble in water, permanent in the air, and neutral to test-paper.

Succinate of Manganese, $C^4H^4Mn''O^4.4H^2O$.—Rhomboïdal prisms or quadrangular tables (triclinic, according to Handl), transparent, amethyst-coloured, neutral, permanent in the air, giving off their water at 100°.

Succinates of Mercury.—α. *Mercuric salts.* Mercuric acetate gives a white precipitate with sodic succinate. A mixture of sodic succinate and mercuric chloride yields, by evaporation, slender needles, apparently consisting of a double salt. Recently precipitated mercuric oxide, boiled with aqueous succinic acid, is partly converted into a white powder, which appears to be a basic succinate.—β. *Mercurous salt.* Alkaline succinates form, with mercurous nitrate, a white precipitate of mercurous succinate, mixed with mercurous nitrate.

Succinate of Nickel, $C^4H^4Ni''O^4.4H^2O$.—The solution of nickel-hydrate in hot aqueous succinic acid deposits this salt, by evaporation over oil of vitriol, in green nodules, soluble in water, acetic acid, and ammonia, insoluble in alcohol. It gives off its water at 130°.

Succinates of Potassium.—The *neutral salt*, $C^4H^4K^2O^4.2H^2O$, forms confused deliquescent crystals, soluble in alcohol, insoluble in ether, giving off their water at 100°.—The *acid salt*, $C^4H^5KO^4.2H^2O$, crystallises readily in transparent regular six-sided prisms, which effloresce slightly in contact with the air. It is very soluble in water, reddens litmus, gives off its water of crystallisation at 100°.—A *hyperacid salt*, $2(C^4H^5KO^4.C^4H^6O^4).3H^2O$ (?), obtained by neutralising a hot solution of 1 pt. succinic acid with carbonate of potassium, and then adding 3 pts. more succinic acid, crystallises on cooling, sometimes without water, sometimes with 9·65 per cent. water of crystallisation. (Fehling.)

Succinates of Silver.—*Argentic salt*, $C^4H^4Ag^2O^4$. Succinate of sodium precipitates nitrate, but not sulphate of silver. The precipitate is white, non-crystalline, of specific gravity 3·518 (**Bödeker**), very slightly soluble in water, and in acetic acid, very soluble in dilute nitric acid, and in ammonia. It becomes coloured at 150°. Chlorine decomposes it immediately. When heated to 100° in a current of hydrogen, it assumes a lemon-yellow colour, and yields a sublimate of succinic acid. The residue consists of *argentous succinate.*

Succinates of Sodium.—The *neutral salt,* $C^4H^4Na^2O^4.6H^2O$, crystallises in prisms with rhombic base, very soluble in water and in alcohol, neutral to test-paper, giving off their water at 100°.—The *acid salt,* $C^4H^5NaO^4.3H^2O$, usually crystallises in flattened prisms, having an acid reaction, slightly efflorescent, and giving off all their water at 100°. They belong to the triclinic system, generally exhibiting the combination: $oP\,.\,\infty{,}P\,.\,\infty P'_{,}\,.\,\infty\breve{P}\infty\,.\,m\,\breve{P}\infty$. Angle $oP : \infty{,}\dot{P} = 128°$; $oP : m\breve{P}\infty = 169° 55'$; $oP : \infty\breve{P}\infty = 140° 50'$; $\infty{,}\dot{P} : \infty\breve{P}\infty = 117° 6'$; $\infty{,}\dot{P} : m{,}\breve{P}n = 115° 8'$; $\infty\breve{P}\infty : m{,}\acute{P}n = 108° 7'$. More rarely small, confused, non-efflorescent crystals are obtained, containing only 2 at. water. When redissolved in water, they yield the salt with 3 at. water.

It has not been found possible to prepare double succinates of sodium and ammonium, or of sodium and potassium.

Succinate of Strontium, $C^4H^4Sr''O^4$ (at 200°).—Precipitated as a white powder, slightly soluble in water, whence it is deposited in the crystalline state on evaporation. According to **Handl** (Wien. Akad. Ber. xxxii. 254), it crystallises in monoclinic prisms, $\infty P\,.\,\infty P\infty\,.\,[\infty P\infty]\,.\,oP$. Angle $\infty P : \infty P$ (clinod.) = 30° 12′; $oP : \infty P\infty = 158°$ (nearly). The crystals are always twins, with $\infty P\infty$ as combination-face. The salt dissolves in acetic and in succinic acid, the latter solution yielding it in the crystalline state when evaporated.

Succinates of Uranium.—The *neutral salt,* $C^4H^4(U^2O^2)''O^4.H^2O$, is obtained in the crystalline state by evaporating to dryness a solution of 4 pts. crystallised uranic nitrate and 1 pt. succinic acid, and washing the residue with a small quantity of water; also by mixing a solution of uranic nitrate with acid succinate of sodium, and evaporating. It is a light-yellow salt, very slightly soluble in water, insoluble in alcohol, not giving off its water till heated to between 230° and 240°. Boiling water extracts succinic acid from it.—*Potassio-uranic succinate,* $C^{12}H^{12}(U^2\overset{''}{O}{}^2)^2K^2O^{12}.H^2O$, is obtained by evaporating a solution of uranic nitrate mixed with excess of neutral potassic succinate: it is then deposited as a light-yellow precipitate, which may be purified by washing with alcohol. It may also be prepared by precipitating uranic nitrate with caustic potash, and digesting the washed precipitate with excess of succinic acid, till it contracts and assumes a light-yellow colour, then evaporating to dryness, and washing with hot alcohol. It is insoluble in water, but is decomposed by continued washing into succinate of potassium, and insoluble basic uranic succinate. It gives off its water at 220°.—*Sodio-uranic succinate,* $C^{12}H^{12}(U^2\overset{''}{O}{}^2)^2Na^2O^{12}$, H^2O, is obtained like the potassium-salt.

Succinate of Yttrium, $2C^4H^4Y''O^4.3H^2O$, is precipitated by succinate of ammonium from acetate of yttrium at the boiling heat (not in the cold), as a lamino-crystalline powder, sparingly soluble in hot and in cold water, insoluble in sal-ammoniac, easily soluble in dilute acids; gives off its water at 100°. (**Popp**, Ann. Ch. Pharm. cxxxi. 179.)

Succinate of Zinc, $C^4H^4Zn''O^4$ (at 200°).—White, anhydrous, crystalline powder, very slightly soluble in water and in succinic acid; easily soluble in mineral acids, acetic acid, ammonia, and potash; insoluble in alcohol. Succinate of sodium does not precipitate chloride of zinc.

SUCCINATES OF ORGANIC BASES.—*Acid Succinate of Cinchonine,* $C^{20}H^{24}N^2O.C^4H^6O^4$, crystallises in long oblique-angled needles, containing $\frac{3}{2}$ at. water, or in large thick crystals containing 1 at. water. Both are easily soluble in water, and melt at 110° (**Hesse**, Ann. Ch. Pharm. cxxii. 226.—*Succinate of Cinchonidine,* $2C^{20}H^{24}N^2O.C^4H^6O^4.6H^2O$, crystallises in long asbestiform prisms, which dissolve in 252 pts. water at 10°; the anhydrous salt crystallises in white nodules (**Hesse**, *ibid.* cxxxv. 342).—*Succinate of Quinine,* $2C^{20}H^{24}N^2O^2.C^4H^6O^4.H^2O$, crystallises from alcohol or from water in long white prisms, soluble in 910 pts. water at 10°, easily soluble in hot water and in alcohol. (**Hesse**, *ibid.* cxxxv. 331.)

Succinate of Urea, $2CH^4N^2O.C^4H^6O^4$, crystallises in monoclinic six-sided prisms, $\infty P\infty\,.\,oP\,.\,\infty P\,.\,\infty P2\,.\,+P\infty\,.\,+P2$. Ratio of axes, $a : b : c = 1 : 1·483 : 1·3646$, Angle of axes $b, c = 83° 28'$; $\infty P\infty : oP = 96° 32'$: $\infty P : \infty P$ (clinod.) = 68° 20′; $\infty P\infty : +P\infty = 129° 4'$. The crystals have a vitreous lustre, are unsymmetrical at the two ends, and generally have but imperfectly developed faces; they cleave imperfectly parallel to +P2. [J. Lischmidt, Wien. Akad. Ber. lii. (2 Abth.), 238.]

Derivatives of Succinic Acid.

No chlorinated substitution-products have hitherto been obtained from succinic acid. By the action of chlorine on citric acid, however, Plantamour obtained an oily body (perhaps $C^4Cl^4O^2.Cl^2$.), which when treated with alcoholic potash yielded a potassium-salt having the composition of potassic tetrachlorosuccinate, $C^4Cl^4K^2O^4$; it is not, however, known whether the acid of this salt is really a derivative of succinic acid. (See CITRIC ACID, i. 996.)

Bromosuccinic Acids.—Two of these acids are known, viz. mono- and di-bromosuccinic acid, both of which may be produced by the direct action of bromine on succinic acid.

MONOBROMOSUCCINIC ACID, $C^4H^3BrO^4 = \left.\begin{matrix}(C^4H^3BrO^2)''\\ H^2\end{matrix}\right\}O^2$. (Kekulé, Ann. Ch. Pharm. cxvii. 125.)—The conditions under which this acid is formed are not exactly known. When succinic acid is heated with bromine and water in a sealed tube, dibromosuccinic acid is generally produced, even when the bromine and succinic acid are mixed in the proportions required to form the monobrominated acid. The formation of the latter appears, however, to be promoted by the presence of a quantity of water, larger than that which is most favourable to the production of dibromosuccinic acid. Carius (Ann. Ch. Pharm. cxxix. 6) prepares the monobrominated acid by slowly heating 5 grms. succinic acid with 2½ c.c. bromine and 40 c.c. water, to 120° in sealed tubes, and obtains it pure by one recrystallisation. Even when quite pure succinic acid is used, a small quantity of a heavy brominated oil is likewise produced, having the composition $C^2H^3Br^3$.

Monobromosuccinic acid is very soluble in water, and crystallises in small nodular aggregates. After neutralisation, it throws down from a solution of silver-nitrate a white silver-salt, which quickly decomposes, with formation of silver-bromide. On adding silver-oxide to the aqueous solution, bromide of silver is quickly formed, and the solution contains malic acid.

According to these reactions, monobromosuccinic acid may be regarded, on the one hand, as a substitution-product of succinic acid, on the other as the bromide of malic acid, forming, as it were, the stepping-stone from succinic to malic acid:

$$\underset{\text{Succinic acid.}}{\left.\begin{matrix}(C^4H^4O^2)''\\ H^2\end{matrix}\right\}O^2} \qquad \underset{\text{Monobromosuccinic acid.}}{\left.\begin{matrix}(C^4H^3BrO^2)''\\ H^2\end{matrix}\right\}O^2,\ \text{or}\ \left.\begin{matrix}(C^4H^3O^2)'''\\ H^2\end{matrix}\right\}\begin{matrix}Br\\ O^2\end{matrix}} \qquad \underset{\text{Malic acid.}}{\left.\begin{matrix}(C^4H^3O^2)'''\\ H^3\end{matrix}\right\}O^3}.$$

These relations are analogous to those which exist between acetic acid, $C^2H^4O^2$, monochloracetic acid, $C^2H^3ClO^2$, and glycollic acid, $C^2H^4O^3$.

DIBROMOSUCCINIC ACID, $C^4H^4Br^2O^4 = \left.\begin{matrix}(C^4H^2Br^2O^2)''\\ H^2\end{matrix}\right\}O^2$. (Kekulé, Ann. Ch. Pharm. cxvii. 123; Suppl. i. 131.—Perkin and Duppa, Chem. Soc. Qu. J. xiii. 102.)—Prepared: 1. By heating 12 grms. of succinic acid, 11 c.c. bromine, and 12 grms. water, in sealed tubes, to about 180°, and crystallising the solid portion of the contents of the tube from boiling water, with addition of animal charcoal* (Kekulé). —2. By the action of water on chloride of dibromosuccinyl, $C^4H^2Br^2O^2.Cl^2$ (Perkin and Duppa).—3. From fumaric acid, $C^4H^4O^4$, by direct addition of bromine. (Kekulé.)

Dibromosuccinic acid crystallises in colourless, mostly opaque prisms, sparingly soluble in cold, easily in boiling *water*, also in *alcohol* and *ether*. When heated with *bromine* and water, it is decomposed with formation of bromoform:

$$C^4H^4Br^2O^4 + 2H^2O + 3Br^2 = CH^3Br^3 + 3CO^2 + 5HBr.$$

By *sodium-amalgam* it is reconverted into succinic acid.

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* The mother-liquor, from which the dibromosuccinic acid has crystallised, contains dibromomaleic acid, $C^4H^2Br^2O^4$, and two isomers of monobromomaleic acid, $C^4H^3BrO^4$ (iii. 788). The dibromomaleic acid volatilises with the vapour of water on distilling the mother-liquor in a retort; the other two acids separate from the mother-liquor on repeated evaporation, and may be purified by fractional crystallisation.—*Metabromomaleic acid*, $C^4H^3BrO^4$, forms large, well-defined, apparently trimetric crystals; melts at 126°—127°, volatilises even below 100°, and dissolves very easily in water, alcohol, and ether. Its *silver-salt*, $C^4HAg^2BrO^4$, separates from a mixture of the acid with silver-nitrate, on addition of ammonia, as a curdy precipitate; the *lead-salt*, $C^4HPb''BrO^4$ (at 100°), is a white precipitate, insoluble in the free acid, but soluble in a large quantity of neutral lead-acetate.—*Parabromomaleic acid*, $C^4H^3BrO^4$, separates in large crystals, apparently triclinic. It is likewise easily soluble in water, alcohol, and ether, and melts at 172°. Its *silver-salt*, $C^4HAg^2BrO^4$, is obtained as a granulo-crystalline precipitate, on mixing the acid with nitrate of silver. It dissolves in boiling water, and more readily in dilute nitric acid.—The *lead-salt*, $C^4HPb''BrO^4.2H^2O$, is soluble both in excess of the acid and in acetate of lead. (Kekulé, Ann. Ch. Pharm. cxxx. 1.)

Dibromosuccinic acid is dibasic. Its salts are easily decomposed by heat, so that, in preparing them, it is necessary to guard against rise of temperature. They are all decomposed by boiling with water, or with excess of base, yielding a metallic bromide, together with another product of decomposition, varying according to the nature of the base. The bromine thus withdrawn (1 or 2 at.) is either replaced by the water-residue, HO, or merely separates in combination with an equivalent quantity of hydrobromic acid, leaving a residue containing 1 at. bromine and 1 at. hydrogen less. Of the decompositions expressed by the following equations, the first three have actually been effected:

$$\begin{array}{llllll}
C^4H^4Br^2O^4 & + \; H^2O & = & HBr & + & C^4H^5BrO^5 \text{ Monobromomalic acid.} \\
C^4H^4Br^2O^4 & & = & HBr & + & C^4H^3BrO^4 \text{ Monobromomaleic acid.} \\
C^4H^4Br^2O^4 & + \; 2H^2O & = & 2HBr & + & C^4H^6O^6 \text{ Tartaric acid.} \\
C^4H^4Br^2O^4 & & = & 2HBr & + & C^4H^2O^4 \text{ (unknown).}
\end{array}$$

Generally, however, several of these reactions take place simultaneously, so that the principal product formed according to one of these four equations, is accompanied by a secondary product formed according to another. Thus *sodic dibromosuccinate*, boiled in aqueous solution, is converted chiefly into acid sodic monobromomalate. On boiling an aqueous solution of *baric dibromosuccinate*, acid baric monobromomaleate is obtained as the chief product of decomposition, together with a small quantity of tartrate.—When *calcic dibromosuccinate* is boiled with water, and lime-water is added till the liquid no longer turns acid after prolonged boiling, the chief product is an insoluble calcium-salt having the composition of the tartrate.—Lastly, *argentic dibromosuccinate* is easily decomposed by boiling with water, yielding (inactive) tartaric acid.

From these reactions, and its mode of formation, dibromosuccinic acid may be regarded either as a substitution-product of succinic acid, or as the bromide of monobromomalic acid, or lastly as a bromide of tartaric acid. It is related to succinic, monobromomalic, and tartaric acids, in the same manner as dibromacetic acid to acetic, monobromoglycollic, and glyoxylic acids (Kekulé's *Lehrbuch*, ii. 33):

$$\begin{array}{lll}
\text{Dibromosuccinic acid, } \left.\begin{array}{r}(C^4H^4Br^2O^2)''\\ H^2\end{array}\right\}O^2 & \left.\begin{array}{r}(C^4H^4O^2)''\\ H^2\end{array}\right\}O^2. & \text{Succinic acid.} \\
\text{”} \quad \left.\begin{array}{r}(C^4H^2BrO^2)'''\\ H^2\end{array}\right\}\begin{array}{l}Br\\ O^2\end{array} & \left.\begin{array}{r}(C^4H^2BrO^2)'''\\ H^3\end{array}\right\}O^3. & \begin{array}{l}\text{Monobromo-}\\ \text{malic acid.}\end{array} \\
\text{”} \quad \left.\begin{array}{r}(C^4H^2O^2)''''\\ H^2\end{array}\right\}\begin{array}{l}Br^2\\ O^2\end{array} & \left.\begin{array}{r}(C^4H^2O^2)''''\\ H^4\end{array}\right\}O^4. & \text{Tartaric acid.}
\end{array}$$

Neutral Dibromosuccinate of Ammonium, $C^4H^2(NH^4)^2Br^2O^4$, crystallises by spontaneous evaporation in large transparent crystals.—The *neutral sodium-salt*, $C^4H^2Na^2Br^2O^4.4H^2O$, is very soluble in water, and remains in small crystals on evaporation; from alcohol it crystallises in shining laminæ.—The *acid potassium-salt* is white, crystalline, and sparingly soluble.—The *calcium-salt*, $C^4H^2Ca''Br^3O^4$, obtained by double decomposition, separates gradually as a crystalline precipitate.—The *silver-salt*, $C^4H^2Ag^2Br^2O^4$, prepared in like manner, is a white powder, insoluble in water.

Ethylic Dibromosuccinate, $C^4H^2(C^2H^5)^2Br^2O^4$, obtained by passing hydrochloric acid gas into an alcoholic solution of the acid and precipitating with water, is very slightly soluble in water, easily soluble in alcohol and ether, and crystallises in long white needles, which melt at 58°, and boil with partial decomposition between 140° and 150°. (Kekulé.)

Dibromosuccinic Anhydride, $(C^4H^2Br^2O^2)''O$, is obtained by heating maleic anhydride, $C^4H^2O^3$, with dry bromine to 100°, for half or three-quarters of an hour. Two atoms of bromine are then taken up, and a yellow liquid is formed, which gradually solidifies to a crystalline mass, to be freed from adhering hydrobromic acid by leaving it, when pulverised, over quicklime. Dibromosuccinic anhydride, thus produced, crystallises from carbonic disulphide in colourless laminæ. It melts at 100°, and is resolved at 180° into hydrobromic acid and bromomaleic anhydride, C^4HBrO^3. With cold water it forms at first a solid mass, which dissolves in a larger quantity of water, and the solution yields, by spontaneous evaporation, a crystallised acid, formed from the anhydride by addition of water, and having the composition, but not the properties, of dibromosuccinic acid, viz.:

Isodibromosuccinic Acid, $C^4H^4Br^2O^4$.—This acid forms large, transparent, well-developed crystals, much more soluble in water than dibromosuccinic acid. It melts at 160°, and is resolved at 180°, or by boiling its aqueous solution, into hydrobromic acid and isobromomaleic acid, $C^4H^3BrO^4$; whereas ordinary dibromosuccinic acid is not decomposed by boiling with water, but when heated by itself is completely decomposed without previous fusion. On boiling the aqueous solution with baryta, *baric isodibromosuccinate* is obtained, which forms warty crystals, and yields isodibromosuccinic acid when decomposed by sulphuric acid.—The *silver-salt* resembles that of ordinary dibromosuccinic acid. (Kekulé, Ann. Ch. Pharm. Suppl. ii. 85.)

SUCCINIC AMIDES. Succinic acid, like other acids of the series $C^nH^{2n-2}O^4$, is capable of forming four normal amides, derivable, but not always directly producible, from the acid and neutral ammonium-salts, by abstraction of water, viz.:

$$\text{Succinamic acid, } C^4H^7NO^3 = \left.\begin{matrix}H^2\\(C^4H^4O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix} = C^4H^5(NH^4)O^4 - H^2O.$$

$$\text{Succinimide, } C^4H^5NO^2 = \left.\begin{matrix}(C^4H^4O^2)''\\H\end{matrix}\right\}N = C^4H^5(NH^4)O^4 - 2H^2O.$$

$$\text{Succinamide, } C^4H^8N^2O^2 = \left.\begin{matrix}(C^4H^4O^2)''\\H^4\end{matrix}\right\}N^2 = C^4H^4(NH^4)^2O^4 - 2H^2O.$$

$$\left.\begin{matrix}\text{Succinonitrile}\\\text{(Cyanide of Ethylene)}\end{matrix}\right\}C^4H^4N^2 = (C^2H^4)''Cy^2 = C^4H^4(NH^4)^2O^4 - 4H^2O.$$

The first three of these compounds contain hydrogen-atoms replaceable by metals or alcohol-radicles. There is also a trisuccinamide, $(C^4\overset{''}{H}{}^4O^2)^3N^2$, formed by the action of succinic chloride on argentic succinimide.

Succinamic Acid. $C^4H^7NO^3 = \left.\begin{matrix}H^2\\(C^4H^4O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (R. Teuchert, Ann. Ch. Pharm. cxxxiv. 136; Bull. Soc. Chim. 1866, i. 286.)—The barium-salt of this acid, $C^8H^{12}Ba''N^2O^6$, is obtained by leaving a slightly warmed solution of succinimide and baric hydrate, in equivalent proportions, to evaporate in a vacuum over oil of vitriol, and repeatedly crystallising the residue from an aqueous solution mixed with alcohol. It forms concentric groups of needle-shaped crystals, easily soluble in water, insoluble in absolute alcohol and in ether, somewhat soluble in aqueous alcohol. The aqueous solution decomposes when kept, and more quickly on boiling, into ammonia and succinate of barium, which is precipitated. With potash, the solution gives off ammonia even in the cold.

By carefully decomposing the barium-salt with somewhat less than the equivalent quantity of sulphuric acid, and evaporating the filtrate, impure succinamic acid (containing baryta) is obtained in rectangular prisms; if the whole of the baryta be precipitated, nothing but succinate of ammonium remains dissolved.

Succinamate of Cadmium, $C^8H^{12}Cd''N^2O^6.H^2O$, remains on precipitating the solution of the barium-salt with sulphate of cadmium, and evaporating the filtrate; it is very soluble in water, insoluble in alcohol, and forms a radiated crystalline mass, or small well-developed rhombic prisms.—The *cupric salt*, $C^8H^{12}Cu''N^2O^6$, prepared in like manner, forms dark-green, microscopic, rhombic laminæ, insoluble in alcohol, slightly soluble in water, and decomposed by boiling with water, with separation of cupric oxide and cupric succinate.—The *lead-salt*, $C^8H^{12}Pb''N^2O^6$, is obtained by heating a solution of succinimide with excess of lead-oxide, and adding alcohol to the filtrate previously treated with carbonic acid, in large, concentrically grouped, easily soluble needles.—The *magnesium-salt*, $C^8H^{12}Mg''N^2O^6.3H^2O$, prepared like the cadmium-salt, is a radiated, nodular, crystalline mass, which by solution and spontaneous evaporation, yields well-developed crystals belonging to the trimetric system.—The *manganous salt*, $C^8H^{12}Mn''N^2O^6.5H^2O$, remains on evaporation as a rose-coloured syrup, which gradually solidifies to a warty or radiate crystalline mass.

The *silver-salt*, $C^4H^6AgNO^3$, is obtained, by mixing the concentrated solutions of argentic nitrate and baric succinamate, as a white crystalline precipitate, and on leaving the filtrate to itself, in prismatic crystals probably belonging to the monoclinic system. It blackens quickly on exposure to light, is easily soluble in ammonia, sparingly in water, and insoluble in alcohol; in boiling water it becomes covered with a black crust.*

Succinamate of Zinc, $C^8H^{12}Zn''N^2O^6$, prepared like the cadmium-salt, forms stellate groups of prisms, easily soluble in water, nearly insoluble in hydrated alcohol, quite insoluble in absolute alcohol.

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* Laurent and Gerhardt (Ann. Ch. Pharm. lxxii. 291), by boiling argentic succinimide with dilute ammonia, obtained a silver-salt, which they regarded as argentic succinamate. It differed, however, in its properties from that above described, being easily soluble in water, and yielding succinamide when decomposed by hydrochloric acid, whereas succinamate of silver thus treated should yield acid succinate of ammonium. According to Teuchert, the salt obtained by Laurent and Gerhardt was probably a hydrated argentic succinimide isomeric with the succinamate (p. 461).

Phenylsuccinamic or *Succinanilic Acid*, $C^{10}H^{11}NO^3 = \left.\begin{matrix}C^6H^5.H\\(C^4H^4O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}.$ (Laurent and Gerhardt, Ann. Ch. Phys. [3], xxiv. 179.)—Obtained by dissolving succinanil in boiling dilute ammonia mixed with a little alcohol, boiling the liquid to expel the latter, and neutralising with nitric acid. The succinanilic acid is then deposited on cooling, in elongated laminæ, which are to be purified by crystallisation from alcohol. It is very slightly soluble in cold, more soluble in hot water: the solution reddens litmus. It melts when heated, and decomposes, at a higher temperature, into water and phenylsuccinimide, which sublimes. It dissolves in ammonia and in potash, and when fused with potash at a gentle heat, gives off aniline.

Succinanilate of Ammonium is very soluble in water, and crystallises in confused masses. The solution does not precipitate *chloride of calcium*, and scarcely produces any turbidity with *chloride of barium*; with *cupric salts* it forms a light-blue, and with *ferrous salts* a yellowish-white precipitate; with *nitrate of silver*, a white precipitate of argentic succinanilate, $C^{10}H^{10}AgNO^3$.

Succinamide, $C^4H^8N^2O^2 = \left.\begin{matrix}(C^4H^4O^2)''\\H^4\end{matrix}\right\}N^2.$ (D'Arcet, Ann. Ch. Pharm. xvi. 215)—This compound separates in small white crystals, on mixing ethylic succinate with strong aqueous ammonia. It dissolves in boiling water, but is nearly insoluble in cold water, also in alcohol and in ether. It melts when heated, and is resolved at about 200° into ammonia and succinimide, $C^4H^5NO^2$. It is easily decomposed by boiling with alkalis. By the action of nitrous acid (*i.e.* by passing nitric oxide into a solution of succinamide in nitric acid), it is resolved, after the manner of amides in general, into succinic acid, water, and nitrogen:

$$C^4H^8N^2O^2 + N^2O^3 = C^4H^6O^4 + H^2O + 2N^2.$$

Phenylsuccinamide or *Succinanilide*, $C^{16}H^{16}N^2O^2 = \left.\begin{matrix}(C^4H^4O^2)''\\(C^6H^5)^2\\H^2\end{matrix}\right\}N^2.$ (Laurent and Gerhardt, Ann. Ch. Phys. [3], xxiv. 179.)—Remains undissolved when the product of the action of succinic acid on anhydrous aniline is exhausted with boiling water; produced also by the action of aniline on succinic chloride. It dissolves easily in boiling alcohol, and is deposited therefrom in tufts of microscopic needles. It is less fusible than succinamide. When melted with potash at a gentle heat, it gives off aniline.

Succinimide, $C^4H^5NO^2 = \left.\begin{matrix}(C^4H^4O^2)''\\H\end{matrix}\right\}N.$ *Bisuccinamide.* (D'Arcet, Ann. Ch. Phys. [2], lviii. 294.—Fehling, Ann. Ch. Pharm. xlix. 198.—Laurent and Gerhardt, Compt. Chim. 1849, p. 108).—Formed: 1. By heating succinamide or succinate of ammonium.—2. By the action of dry ammonia-gas on succinic anhydride:

$$(C^4H^4O^2)''O + NH^3 = H^2O + (C^4H^4O^2)''HN.$$

Succinimide crystallises in large transparent crystals, $C^4H^5NO^2.H^2O$, which give off their water even on exposure to the air. It is easily soluble in water and in alcohol, less soluble in ether; melts at 210°, and sublimes without alteration.

The hot alcoholic solution of succinimide, mixed with a small quantity of ammonia, and then with nitrate of silver, yields on cooling, large crystals of *argentic succinimide*, $C^4H^4O^2AgN$. This compound detonates when heated, and when triturated with sal-ammoniac, is converted, with evolution of ammonia, into argentic chloride and succinimide. By prolonged boiling with water, it yields argentic succinate. When boiled with water containing a few drops of ammonia, it is converted, according to Laurent and Gerhardt, into argentic succinamate. Teuchert, however (p. 460), obtained by this process a hydrated argentic succinimide, $2C^4H^4O^2AgN.H^2O$, and is of opinion that Laurent and Gerhardt's compound was also a hydrated argentic succinimide, containing $C^4H^4O^2AgN.H^2O$, isomeric therefore with argentic succinamate.

A solution of argentic succinimide in a small quantity of ammonia, leaves, on spontaneous evaporation, an alkaline syrupy liquid, which solidifies after some time to a mass of hard brittle crystals, consisting of *argentammonium-succinimide*, $C^4H^4O^2(NH^3Ag)N$, which is distinguished from argentic succinimide by its property of giving off ammonia when treated with potash at ordinary temperatures.

Chlorosuccinimide.—Ethylic perchlorosuccinate (p. 463) is converted by ammonia into a crystallisable and sublimable body, probably consisting of tetrachlorosuccinimide, $C^4Cl^4O^2HN$. The analysis of this body does not agree very well with this formula, but the formation of trichloracetamide, at the same time, seems to show that it is produced in the manner shown by the equation:

$$\underset{\substack{\text{Ethylic per-}\\\text{chlorosuccinate.}}}{C^8Cl^{14}O^4} + 3NH^3 = 4HCl + \underset{\text{Trichloracetamide.}}{2C^2H^2Cl^3NO} + \underset{\substack{\text{Tetrachlorosuc-}\\\text{cinimide.}}}{C^4Cl^4O^2HN}.$$

On treating the product with ether, the tetrachlorosuccinimide and trichloracetamide dissolve, while sal-ammoniac remains behind; and the ethereal solution leaves on evaporation, a residue, from which cold water extracts an ammoniacal compound of tetrachlorosuccinimide (chlorazosuccate of ammonium), leaving the trichloracetamide. The aqueous solution, mixed with hydrochloric or nitric acid, deposits the tetrachlorosuccinimide in four-sided prisms. It is nearly insoluble in water, very soluble in alcohol and ether; melts in water between 83° and 85°, in the air at 200°; sublimes at 125°, and turns yellow at 250°. It decomposes carbonates, and its ammoniacal solution precipitates the salts of calcium and copper. Its ammoniacal solution evaporates over the water-bath, decomposes with brisk effervescence, and yields, among other products, a crystalline substance, regarded by Gerhardt as **chlorosuccilamide**, $C^3H^2Cl^3NO^2$, the amide of chlorosuccic acid (p. 463), possibly thus:

$$\underset{\substack{\text{Chlorosuccini-}\\\text{mide.}}}{C^4Cl^4O^2HN} + H^2O = CO^2 + HCl + \underset{\substack{\text{Chlorosuccila-}\\\text{mide.}}}{C^3H^2Cl^3NO}.$$

Phenylsuccinimide, or *Succinanil*, $C^{10}H^9NO^2 = \left.\begin{matrix}(C^4H^4O^2)''\\ C^6H^5\end{matrix}\right\}N$. (Laurent and Gerhardt, Ann. Ch. Phys. [3], xxxiv. 179.)—Obtained by heating pulverised succinic acid with dry aniline, and treating the crystalline mass with boiling water, which dissolves the greater part of it, consisting of succinanil, and leaves a residue of succinanilide. The succinanil crystallises on cooling in colourless laminæ, and by recrystallisation from alcohol it may be obtained quite puro, in fine long interlaced needles. It appears to be sublimable without decomposition. It is insoluble in cold water. Aqueous potash has no action upon it, but when heated with solid potash it gives off aniline. Boiling aqueous ammonia converts it into succinanilic acid (p. 460).

Trisuccinamide, $(C^4\overset{\prime}{H}{}^4O^2)^3N^2$. (Chiozza and Gerhardt, Ann. Ch. Pharm. xc. 108.)—Produced, together with argentic chloride, by treating argentic succinimide with an ethereal solution of succinic chloride:

$$2(C^4H^4O^2)''AgN + (C^4H^4O^2)''Cl^2 = 2AgCl + (C^4\overset{\prime\prime}{H}{}^4O^2)^3N^2.$$

It is slightly soluble in ether, easily soluble in absolute alcohol, and crystallises in small triangular plates which melt at 83°. By aqueous alcohol it is quickly decomposed, yielding succinic acid, ethylic succinate, and succinimide.

SUCCINIC ANHYDRIDE. $C^4H^4O^3 = (C^4H^4O^2)''O$. *Anhydrous Succinic Acid*. (D'Arcet, Ann. Ch. Phys. [2], lviii. 282.—Gorhardt and Chiozza, Compt. rend. xxxvi. 1050.—Kraut, Ann. Ch. Pharm. cxxxvii. 254.)—Obtained: 1. By boiling succinic acid very rapidly in a retort, and absorbing the water as fast as it condenses.—2. By distilling succinic acid once or twice with phosphoric anhydride (D'Arcet).—3. By heating the acid with phosphoric pentachloride:

$$C^4H^6O^4 + PCl^5 = 2HCl + POCl^3 + C^4H^4O^3.$$

—4. By heating ethylic succinate with chlorobenzene. (Kraut, p. 463.)

Succinic anhydride is a white mass, less soluble in *water*, but more soluble in *alcohol*, than succinic acid. It dissolves in boiling absolute alcohol, apparently without formation of ethylic succinate, and is deposited from the solution in long needles. It is very little soluble in *ether*, either cold or boiling. Melts at 119·6° (Kraut). By solution in boiling water, it is reconverted into succinic acid. With dry *ammonia-gas* it becomes hot, and forms succinimide, together with water:

$$C^4H^4O^2.O + NH^3 = H^2O + C^4H^4O^2.HN.$$

With *phosphoric pentachloride*, it yields succinic chloride and phosphoric oxychloride:

$$C^4H^4O^2.O + PCl^5 = POCl^3 + C^4H^4O^2Cl^2.$$

SUCCINIC CHLORIDE, or *Chloride of Succinyl*, $(C^4H^4O^2)''Cl^2$. (Gerhardt and Chiozza, *loc. cit.*)—Produced as above, by distilling succinic anhydride with phosphoric pentachloride, and purified by rectification. It is a fuming, strongly refracting liquid, boiling at about 190°. With water it easily yields succinic acid; with alcohol, ethylic succinate.

Dibromosuccinic Chloride, $C^4H^2Br^2O^2.Cl^2$, is obtained by heating succinic chloride with bromine to 120°—130°, for three or four hours (Perkin and Duppa, Chem. Soc. Qu. J. xiii. 102); also by direct addition of bromine to fumaric chloride, $C^4H^2O^2Cl^2$ (Kekulé). It is a liquid, which boils at 220° (Kekulé), and is converted by water into dibromosuccinic acid. (Perkin and Duppa.)

SUCCINIC ETHERS. *a.* Of succinic ethers containing monatomic alcohol-radicles, only the neutral methylic, ethylic, cetylic, and benzhydrolic ethers have hitherto been obtained.

Methylic Succinate, $C^6H^{10}O^4 = \left.\begin{matrix}(C^4H^4O^2)''\\(CH^3)^2\end{matrix}\right\}O^2$, is produced by passing hydrochloric acid gas into a solution of succinic acid in methylic alcohol. When purified in the usual way, it forms a crystalline mass, melting at 20°, and solidifying again at 16°. It is nearly insoluble in water, but dissolves in alcohol and ether; boils at 198°. Specific gravity of liquid = 1·179 at 20°; of vapour 5·29. (Fehling, Ann. Ch. Pharm. xlix. 195.)

Ethylic Succinate, $C^8H^{14}O^4 = \left.\begin{matrix}(C^4H^4O^2)''\\(C^2H^5)^2\end{matrix}\right\}O^2$.—Prepared like the methylic ether, or by distilling 10 pts. succinic acid, 20 pts. alcohol, and 5 pts. strong hydrochloric acid, and purifying the oily product by distillation over massicot (D'Arcet, Ann. Ch. Phys. [2], lviii. 291); also by dropping alcohol into a retort in which succinic acid is heated to a temperature near its boiling-point (Gaulthier de Clanbry). It is an oil, slightly soluble in water, boiling at 214°, and burning with a yellow flame. Specific gravity of liquid = 1·036; of vapour = 6·22. (D'Arcet.)

When potassium is introduced into ethylic succinate, the liquid becomes hot, gives off hydrogen, and forms a pasty mass, from which, after treatment with water and crystallisation of the undissolved portion, yellowish laminæ are obtained, having the composition $C^6H^8O^3$ [therefore, perhaps, *ethylsuccinic anhydride*, $C^4H^3(C^2H^5)O^3$]. The crystals melt at 133°; sublime at 206°; and are decomposed by alkalis into alcohol and an alkaline succinate. With ammonia they form a light-yellow substance, crystallising in needles (Fehling, Ann. Ch. Pharm. xlix. 192). Respecting the rational formula, see Geuther. (Zeitschr. Ch. Pharm. 1866, p. 5.)

Ethylic succinate heated with chlorobenzene (chloride of phenyl) in a sealed tube to 250°, for several hours, yields ethylic chloride, ethylic benzoate, and succinic anhydride (Kraut, Ann. Ch. Pharm. cxxxvii. 254):

$$\left.\begin{matrix}(C^4H^4O^2)''\\(C^2H^5)^2\end{matrix}\right\}O^2 + C^7H^5OCl = C^2H^5Cl + \left.\begin{matrix}C^7H^5O\\C^2H^5\end{matrix}\right\}O + (C^4H^4O^2)''.O.$$

Substitution-products of Ethylic Succinate (Cahours, Ann. Ch. Pharm. xlvii. 29; Malaguti, *ibid.* lvi. 291).—When ethylic succinate is saturated with chlorine, and then exposed to sunshine in a bottle filled with chlorine-gas, a crystallisable substance is formed, which melts at 115°—120°, has the composition $C^8HCl^{13}O^4$, and may therefore be regarded as ethylic succinate in which all the hydrogen, except one atom, is replaced by chlorine. By distillation it is resolved, at about 290°, into carbonic anhydride, chloride of trichloracetyl, trichloride of carbon, and probably chlorosuccide, C^3HCl^3O:

$$C^8HCl^{13}O^4 = CO^2 + C^2Cl^3O.Cl + C^2Cl^6 + C^3HCl^3O.$$

With alcohol it yields neutral ethylic carbonate (i. 800), ethylic trichloracetate (i. 879), hydrochloric acid, and the ethylic ether of chlorosuccic acid.—The chlorinated ether, or the product formed from it by the action of alcohol, yields, when treated with potash, carbonate, chloride, formate, and chlorosuccate of potassium. (Malaguti.)

Laurent and Gerhardt suppose that Malaguti's chlorinated ether contains no hydrogen, but consists of perchlorinated ethylic succinate, $C^8Cl^{14}O^4$. Gerhardt regards chlorosuccic acid as $C^4HCl^3O^2 = \left.\begin{matrix}C^3Cl^3O\\H\end{matrix}\right\}O$ (trichloracrylic acid), and chlorosuccide as the corresponding chloride, $C^3Cl^3O.Cl$. These formulæ afford simple explanations of all the reactions, but they do not agree well with the analytical numbers obtained by Cahours and Malaguti.—Chlorinated ethylic succinate, treated with ammonia, yields, among other products, a compound designated by Malaguti as chlorazosuccic acid (C^3HCl^3ON), but regarded by Laurent as tetrachlorosuccinimide, $C^4Cl^4O^2.HN$ (p. 461). For further details respecting these chlorinated compounds, see Gerhardt's *Traité*, ii. 466, 477.

Cetylic Succinate, $C^{36}H^{70}O^4 = \left.\begin{matrix}(C^4H^4O^2)''\\(C^{16}H^{33})^2\end{matrix}\right\}O^2$. (Tüttscheff, Rep. Chim. pure, ii. 463.)—Produced by heating 1 at. succinic acid and 2 at. ethal for 15 hours (to what temperature?). Crystallises from hot ether-alcohol in white laminæ, melting at 58°, slightly soluble in alcohol, more soluble in ether.

Benzhydrolic Succinate, $C^{30}H^{26}O^4 = \left.\begin{matrix}(C^4H^4O^2)''\\(C^{13}H^{11})^2\end{matrix}\right\}O^2$.—Produced by heating succinic acid with benzhydrol; described under Phenylbenzoyl (iv. 479).

β. *Succinic Ethers containing Diatomic Alcohol-radicles.*

Only two of these ethers have yet been obtained, viz., the acid and neutral succinates of ethylene, both discovered by Lourenzo. (Ann. Ch. Pharm. cxv. 358.)

Ethylene-succinic, or *Glycolsuccinic Acid*, $C^6H^{10}O^5 = \left.\begin{matrix}(C^4H^4O^2)''\\(C^2H^4)''\\H^2\end{matrix}\right\}O^3$.—Produced by heating succinic acid with glycol to 150°: $C^4H^6O^4 + C^2H^6O^2 = C^6H^{10}O^5 + H^2O$.

It forms small crystals, melting below 100°, soluble in water and alcohol, insoluble in ether.

Neutral Ethylenic Succinate, or *Succinate of Glycol*, $C^6H^8O^4 = \left.\begin{matrix}(C^4H^4O^2)''\\(C^2H^4)''\end{matrix}\right\}O^2$, remains when ethylene-succinic acid is heated to 300°, as a crystalline mass, which melts at about 90°, is insoluble in water and in ether, but may be crystallised from boiling alcohol.

SUCCINITE. An amber-coloured variety of lime-garnet. The name is applied also by Breithaupt to amber.

SUCCINONE. This name has been applied to a volatile oil obtained by the distillation of neutral calcic succinate (p. 455).

SUCCINO-SULPHURIC ACID. Syn. with SULPHOSUCCINIC ACID.

SUCCINUM. Syn. with AMBER.

SUCCINYL. $C^4H^4O^2$. The diatomic radicle of succinic acid, &c.

SUCCINYLIC ACID. Syn. with SUCCINIC ACID.

SUCCISTERENE (from *succinum* and *stearin*).—The name applied by Pelletier and Walter to the portion of *Colophonium succini* which is insoluble in alcohol and ether. (See AMBER, i. 163.)

SUCROSE. Syn. with CANE-SUGAR.

SUET. The solid fat of the ox or sheep. Mutton-suet is more solid than beef-suet, and consists mainly of stearin, together with palmitin, and small quantities of olein and hircin; melts at 50° (Arzbächer). Beef-suet contains more stearin than human fat, more palmitin than mutton-suet, and about the same quantity of olein; melts at 47°. (Arzbächer.)

SUGARS. Under this name are included a number of organic compounds, mostly of vegetable origin, which are soluble in water, mostly crystallisable, have a sweet taste, and neutral reaction to vegetable colours, and in the state of solution rotate the plane of vibration of a ray of polarised light. They may be divided into fermentable or true sugars, and non-fermentable sugars or saccharoïds.

A. *Fermentable Sugars.*—These sugars are carbohydrates, represented[*] by the general formula $C^nH^{2p}O^p$, and may be subdivided into the two following groups, the first including those sugars which are directly susceptible of vinous fermentation, the second those which undergo this transformation only after conversion into sugars of the first group:

a. $C^{12}H^{12}O^6$ (Glucoses).

	Molecular rotatory power.
Dextrose or Dextroglucose (ii. 855)	+ 56°
Lævulose or Lævoglucose (ii. 863)	− 106° at 14° − 53° at 90°
Galactose (iii. 1023).	+ 83°

To this group belong also a number of sugars differing more or less in properties from the three preceding, viz. Maltose (iii. 999), Mannitose (iii. 826); the sugar found by Meissner (Jahresb. 1861, p. 800) as a normal constituent of muscular flesh; Dulcitose, a product of the oxidation of dulcite by nitric acid (Carlet, Ann. Ch. Pharm. cxvii. 143); the sugar which Berthelot obtained (ii. 856) from mannite and glycerin by the action of a peculiar ferment; and many of the sugars resulting from the decomposition of natural glucosides under the influence of acids (ii. 865).

b. $C^{12}H^{22}O^{11}$ (Cane-sugar and its isomers).

	Molecular rotatory power.
Saccharose or Cane-sugar	+ 73·8°
Parasaccharose	+ 108°
Lactose or Milk-sugar	+ 59·3
Melezitose (iii. 868)	+ 94
Melitose (iii. 869)	+ 102
Mycose (iii. 1068)	+ 192·5
Trehalose ,,	+ 199

The sugars of this group may be regarded as ethers of the glucoses, being related to them in the same manner as diethylenic alcohol to glycol, or as diglycerin to glycerin (iii. 576, 884):

$$\begin{array}{ccc} \text{Glucose.} & \qquad\qquad & \text{Saccharose.} \\ \left.\begin{array}{c}(C^6H^6)^{vi} \\ H^6\end{array}\right\}O^6 & & \left.\begin{array}{c}(\overset{vi}{C^6H^6})^2 \\ H^{10}\end{array}\right\}O^{11} \end{array}$$

B. *Non-fermentable Sugars* or *Saccharoids.*—Of these bodies, the first four in the following list have the composition of the glucoses; the rest are not carbohydrates, but contain a quantity of hydrogen larger than is sufficient to convert the whole of the oxygen into water:

	Molecular rotatory power.
Eucalyn, $C^6H^{12}O^6$ (ii. 601)	+ 55° (nearly)
Sorbite, $C^6H^{12}O^6$ (v. 352)	− 46·9°
Quercitose,* $C^6H^{12}O^6$? (v. 37)	0°
Inosite, $C^6H^{12}O^6$ (iii. 274)	0°
Mannite, $C^6H^{14}O^6$ (iii. 825)	0°
Dulcite, $C^6H^{14}O^6$ (ii. 348)	0°
Isodulcite,† $C^6H^{14}O^6$ (v. 7)	+ 7·6°
Quercite, $C^6H^{12}O^5$ (v. 6)	+ 33·5° (nearly)
Pinite, $C^6H^{12}O^5$ (iv. 652)	+ 58·6°
Erythromannite, $C^{12}H^{30}O^{12}$ (ii. 504)	0°

In these tables the value of the molecular rotatory power is given for the transition-tint (iii. 672), which is the same as that for the medium yellow ray, and is commonly expressed by the symbol $[\alpha]_j$. The value for the red ray is related to this by the equation:

$$[\alpha]_r = \frac{23}{30}[\alpha]_j$$

The molecular or specific rotatory power $[\alpha]$ is given by one of the following equations:

$$\text{I.}\quad [\alpha] = \frac{\alpha}{\epsilon\,.\,\delta\,.\,\lambda} \quad . \quad . \quad \text{(iii. 673.)}$$

$$\text{II.}\quad [\alpha] = \frac{a\,V}{l\,p} \text{ or } [\alpha] = \frac{a}{v\,l}$$

In these equations, α or a is the observed angle of rotation; ϵ, the concentration of the solution (1 grm. of solution containing ϵ grms. of substance); δ, the specific gravity of the solution; λ or l, the length of the column of liquid in decimetres.‡

Further: p, the weight of the substance in grammes; V, the volume of the solution containing it.

Also: v, the concentration of the solution according to volume, *i.e.* the quantity of grammes of the substance contained in 1 cub. cent. of solution, so that $v = \frac{p}{V} = \epsilon\,.\,\delta$.

The equation I. is used when the concentration and specific gravity of the solution are known; the equation II. when, as is generally the case, the solution is prepared by weighing out the substance, and filling up the liquid with water to a given bulk.

The molecular rotatory power of most sugars is but little affected by temperature; that of lævulose, however, diminishes rapidly as the temperature rises. A recently prepared mixture of crystallised dextrose (grape-sugar) exhibits, when recently prepared, a rotatory power of about 112°; but it decreases gradually at ordinary temperatures, and quickly when the liquid is heated, and ultimately remains constant at + 56°.

Mixtures of dextrose and lævulose exhibit dextro- or lævo-rotation, according to the proportions in which the two are mixed; this is seen in different samples of honey, and in fruits. Inverted sugar (ii. 863), produced by the action of acids on cane-sugar, is a mixture of dextrose and lævulose in equal quantities. Its specific rotatory power varies greatly according to temperature: at 15° it is $[\alpha] = -\frac{106}{2} + \frac{56}{2} =$

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* The sugar obtained by decomposing quercitrin with dilute sulphuric acid is, according to Rigaud (Ann. Ch. Pharm. xc. 195), identical with dextrose in every respect, excepting that it is optically inactive.

† According to Hlasiwetz and Pfaundler, on the other hand (Jahresb. 1864, p. 564), quercitrin thus treated yields a saccharine substance, which they call isodulcite, crystallising in the same form as cane-sugar, but differing therefrom in properties and composition. The crystals contain $C^6H^{12}O^5.H^2O$, and melt, with loss of their crystallisation-water, between 105° and 110°. Isodulcite dissolves in 2·09 pts. water at 15°, and is also readily dissolved by hot absolute alcohol. It reduces an alkaline cupric solution, and forms with nitric acid, a nitro-compound containing $C^6H^9(NO^2)^3O^5$.—Hydrated isodulcite is isomeric with mannite and dulcite; the anhydrous compound with pinite and quercite.

‡ In the equation given under LIGHT (iii. 673), the unit of length for l, is 1 centimetre: and the specific rotatory power of cane-sugar there calculated from the formula is 7·3°, whereas in the table on p. 464, where the unit of length is supposed to be a decimetre, it is ten times as much, namely 73·8°.

$-25°$; at $25°$ it is $-12·5°$; at $90°$ it is nearly $= 0$, and at higher temperatures the mixture becomes dextrorotatory.

Chemical Reactions of Sugars: 1. *Decomposition by heat.*—All sugars are decomposed by heat. Those which contain water of crystallisation give it off at 100° or a little above—viz., grape-sugar, melitose, trehalose, eucalyn, and inosite at 100°, melezitose at 110°, mycose at 130°. At somewhat higher temperatures the glucoses give off more water, and yield anhydrides analogous to mannitan (iii. 823): thus

$$\left.\begin{matrix}\text{Dextrose}\\ \text{Lævulose}\end{matrix}\right\} C^6H^{12}O^6 = \left\{\begin{matrix}H^2O + C^6H^{10}O^5 \text{ Glucosan}\\ H^2O + C^6H^{10}O^5 \text{ Lævolusan.}\end{matrix}\right.$$

When further heated, they yield a number of somewhat indefinite compounds, designated by the general name caramel; and at still higher temperatures, they undergo complete decomposition, giving off carbonic oxide, carbonic anhydride, marsh-gas, acetic acid, aldehyde, acetone, furfurol, liquid hydrocarbons, and other products. The sugars, $C^{12}H^{22}O^{11}$, appear to be first converted by heat into a mixture of glucoses and glucosanhydrides (*e. g.*, cane-sugar into dextrose and lævolusan), which are resolved by further heating into the products above mentioned.

2. *Oxidation.*—Sugars are easily oxidable. With strong oxidising agents they mostly yield products of comparatively simple constitution, such as carbonic, formic, and oxalic acids. Glucose and cane-sugar, &c., distilled with a mixture of *manganic peroxide* or *potassic chromate* and sulphuric acid, or with *peroxide of lead* and water, yield chiefly formic and carbonic acids; milk-sugar distilled with *potassic chromate* and sulphuric acid yields the same products, together with aldehyde.

By prolonged boiling with *strong nitric acid*, sugars yield chiefly oxalic acid. With *more dilute acid*, and at lower temperatures, acids are formed nearer in composition to the sugars—chiefly mucic, saccharic, and tartaric acids, sometimes also racemic acid. The formation of the isomeric compounds, mucic and saccharic acids, is represented by the equation:

$$C^6H^{12}O^6 + O^3 = H^2O + C^6H^{10}O^8.$$

Tartaric acid is probably formed by further oxidation of saccharic acid; and racemic acid by oxidation of mucic acid (p. 35).

Cane-sugar, glucose, and indeed most other sugars, yield by this gradual oxidation, only saccharic acid; milk-sugar yields mucic with a small quantity of saccharic acid; melitose yields saccharic with a small quantity of mucic acid.

Sugars are oxidised by many metallic oxides and salts, and therefore act as reducing agents: thus from *silver-salts*, especially in presence of ammonia, they throw down metallic silver; from *cupric salts*, especially in alkaline solution, they precipitate cuprous oxide (ii. 860). The glucoses in general exert a stronger reducing action than cane-sugar and its isomers; of the latter, milk-sugar reduces more quickly than cane-sugar. The products formed in these reactions have not been very closely investigated. (See Gallactic and Pectolactic Acids, iii. 1024.)

3. *Very strong nitric acid* (specific gravity, 1·525), or a mixture of strong *nitric* and *sulphuric acids*, converts sugars into nitro-compounds: cane-sugar thus treated yields nitro-saccharose, probably $C^{12}H^{18}(NO^2)^4O^{11}$; inosite yields crystallisable nitro-inosite, $C^6H^6(NO^2)^6O^6$; isodulcite, $C^6H^{12}O^5.H^2O$, yields $C^6H^9(NO^2)^3O^5$; dextrose, milk-sugar, and trehalose yield nitro-compounds whose composition has not been exactly ascertained.

4. Reactions with other *acids.*—By boiling with dilute *sulphuric* or *hydrochloric acid*, cane-sugar and its isomers are converted into glucoses:

$$C^{12}H^{22}O^{11} + H^2O = C^6H^{12}O^6 + C^6H^{11}O^6.$$

In this manner melezitose yields 2 at. of dextrose; lactose yields 2 at. of galactose; cane-sugar yields 1 at. dextrose + 1 at. lævulose; and melitose yields 1 at. dextrose + 1 at. eucalyn.

The glucoses offer considerable resistance to further transformation by dilute mineral acids; but ultimately they turn brown and decompose, the more quickly as the acid is less dilute, yielding brown humus-like products of indeterminate composition; this transformation is most quickly effected by strong hydrochloric acid.

Concentrated sulphuric acid acts on the sugars, $C^{12}H^{22}O^{11}$, much more strongly than on the glucoses. A strong syrup of cane- or milk-sugar mixed with concentrated sulphuric acid, is immediately decomposed with great intumescence, evolution of sulphurous anhydride and various volatile products, and separation of a black carbonaceous mass.—Dextrose, on the other hand, mixed with strong sulphuric acid, forms, without blackening, a sulpho-acid, $C^{24}H^{48}SO^{27} = 4C^6H^{12}O^6.SO^3$, the action being exactly similar to that of the organic acids on the glucoses (p. 467):

$$4C^6H^{12}O^6 + H^2SO^4 = H^2O + C^{24}H^{48}SO^{27}.$$

Phosphoric acid appears also to form a similar compound with dextrose.

The glucoses heated with solutions of *organic acids* act like polyatomic alcohols yielding ethereal compounds called saccharides, which resemble the mannitic ethers (ii. 521), inasmuch as they are derivatives, not directly of glucose, $C^6H^{12}O^6$, but of glucosan, $C^6H^{10}O^5$: thus—

$$\underset{\text{Dextrose.}}{C^6H^{12}O^6} + \underset{\text{Butyric acid.}}{2C^4H^8O^2} - 3H^2O = \underset{\text{Dibutyryl-glucosan.}}{C^6H^8(C^4H^7O)^2O^5}$$

$$\underset{\text{Dextrose.}}{C^6H^{12}O^6} + \underset{\text{Stearic acid.}}{2C^{18}H^{36}O^2} - 3H^2O = \underset{\text{Distearyl-glucosan.}}{C^6H^8(C^{18}H^{35}O)^2O^5}$$

$$\underset{\text{Dextrose.}}{C^6H^{12}O^6} + \underset{\text{Acetic acid.}}{6C^2H^4O^2} - 7H^2O = \underset{\text{Hexacetyl-glucosan.}}{C^6H^4(C^2H^3O)^6O^5}$$

$$\underset{\text{Dextrose.}}{C^6H^{12}O^6} + \underset{\text{Alcohol.}}{2C^2H^6O} - 2H^2O = \underset{\text{Diethyl-glucosan.}}{C^6H^8(C^2H^5)^2O^5}{}^*$$

Cane-sugar and its isomers, heated with organic acids, are first converted into glucoses, and then into saccharides as above.

With *tartaric acid*, the sugars appear to form several different compounds. The following are described by Berthelot (*Chim. org.* ii. 294):

1. From Dextrose, $C^6H^{12}O^6 + 4C^4H^6O^6 - 5H^2O = C^{22}H^{26}O^{25}$
2. „ Cane-sugar, $C^6H^{12}O^6 + 2C^4H^6O^6 - 3H^2O = C^{14}H^{18}O^{15}$
3. „ Milk-sugar, $C^6H^{12}O^6 + 4C^4H^6O^6 - 3H^2O = C^{22}H^{30}O^{27}$
4. „ „ $3C^6H^{12}O^6 + 4C^4H^6O^6 - 7H^2O = C^{34}H^{46}O^{35}$

5. *Reactions with Alkalis.*—Sugars act like weak acids, inasmuch as they are capable of forming saline compounds with certain bases, or, in other words, of exchanging part of their hydrogen for metals. Thus dextrose, $C^6H^{12}O^6$, forms with baryta the compound $C^{12}H^{22}Ba''O^{12}$; and cane-sugar forms with the same base, a compound which may be formulated as $C^{12}H^{20}Ba''O^{11}.H^2O$, or as $C^{12}H^{22}O^{11}.Ba''O$. Dextrose and cane-sugar also form saline compounds with potash and soda; these compounds are obtained by agitating the alcoholic solution of the sugar with alcoholic potash.

In aqueous solution, on the other hand, the glucoses are very easily decomposed by alkalis, even when very dilute. The decomposition takes place slowly in the cold, more quickly on heating, the liquid first turning yellow, then brown, and yielding a quantity of indeterminate brown humous substance. Dextrose thus treated yields glucic acid (ii. 848), as the first product of the reaction.

The sugars, $C^{12}H^{22}O^{11}$, are for the most part much less readily attacked by alkalis than the glucoses; they are not attacked by dilute alkaline solutions in the cold, and but slowly even when heated; but they are decomposed by boiling with concentrated alkaline liquids. When fused with caustic alkalis they yield oxalic acid.

In general those sugars (and other carbohydrates), which are most easily attacked by acids, offer the greatest resistance to the action of alkalis.

The sugars and other carbohydrates, when treated with *ammonia* in the form of gas, or of aqueous solution, are capable of forming compounds somewhat resembling gelatin, and containing in some cases as much as 14—19 per cent. nitrogen. Dusart (Compt. rend. lii. 974), by heating glucose, milk-sugar, or starch with aqueous ammonia to 150°, obtained nitrogenised substances, which were precipitated by alcohol in tenacious threads, and formed with tannic acid an insoluble, non-putrefying compound. Similar results were obtained by Schützenberger (Jahresb. 1861, p. 910). P. Thénard (*ibid.* p. 908), by operating in a similar manner, but at a temperature of 280°, obtained yellow or brown nitrogenised products—some soluble, others insoluble in water, and containing as much as 19 per cent. nitrogen. These results are especially interesting in connection with the observation made by Hunt (Jahresb. 1847-48, p. 845), that bone-gelatin has, approximately, the composition of an amide of the carbohydrates:

$$C^6H^{12}O^6 + 2NH^3 = C^6H^{10}N^2O^2 + 4H^2O;$$

and that, on the other hand, gelatin and similar substances, when boiled for some time with sulphuric acid, yield, among other products, sugars resembling glucose.

Action of Ferments.—The glucoses, viz. dextrose, lævulose, and galactose, are directly susceptible of vinous fermentation; that is to say, when their aqueous solutions are placed in contact with yeast at a certain temperature, they are immediately resolved into alcohol and carbonic anhydride: $C^6H^{12}O^6 = 2C^2H^6O + 2CO^2$. Cane-sugar and its homologues, on the other hand, do not undergo this change until they have first been converted into glucoses, this action being due to a peculiar soluble ferment, analogous to diastase, contained in the yeast (p. 471). Respecting the various circumstances attending vinous fermentation, and the action of other ferments on sugars, see FERMENTATION (ii. 623).

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* Produced by heating cane-sugar with ethylbromide and potash.

Most of the sugars enumerated in the preceding tables (pp. 464, 465), have already been described in their alphabetical places. We have here to consider in detail the one to which the name sugar is especially applied, viz.:

CANE-SUGAR OR SACCHAROSE.*

This kind of sugar is very widely diffused in the vegetable kingdom, and has been lately shown to exist in many plants, from which, in consequence of the modes of extraction formerly adopted, only grape-sugar (dextrose), or uncrystallisable fruit-sugar (a mixture of dextrose and lævulose), had been obtained. It is very abundant in the stems of certain grasses, especially in the sugar-cane (*Saccharum officinarum*), which contains more than 20 per cent. of it, unmixed with any other kind of sugar, and the sorgho or Chinese sugar-cane (*Sorghum saccharatum*, p. 354), which contains it to the amount of 9 to 9½ per cent. The juice of maize-stems, cut shortly after flowering, contains a quantity of sugar amounting to between 7·4 and 7·9 per cent. of the juice, and about half consisting of cane-sugar (Lüdersdorff).—Cane-sugar is abundant in many fleshy roots, as those of the carrot and parsnip, and especially in that of beet (*Beta vulgaris*), which contains on the average from 7 to 11 per cent. of it, sometimes as much as 14 per cent.; and in the stems of certain species of birch and maple, especially of the sugar-maple (*Acer saccharinum*), and of many kinds of palm. (See PALM-SUGAR, iv. 336.)

Most sweet fruits contain cane-sugar together with inverted sugar (ii. 863); some, as walnuts, hazelnuts, almonds, coffee-beans, and St. John's-bread (the fruit of *Ceratonia siliqua*), contain only cane-sugar. Honey and the nectars of flowers contain cane-sugar together with inverted sugar; the sugar in the nectars of cactuses is almost wholly cane-sugar.

Manna from Sinai (the produce of *Tamarix mannifera*) contains 55 per cent. cane-sugar, 25 inverted sugar, and 20 dextrin, &c. Manna from Kurdistan contains 61 per cent. cane-sugar, 16·5 inverted sugar, and 22·5 dextrin, &c. (Berthelot, Compt. rend. liii. 583.)

Cane-sugar has been known in India and China from very early times, and in Europe since the time of Alexander the Great. The culture of the sugar-cane was imported, in the fourteenth and fifteenth centuries, from Nubia, Arabia, and Egypt, into Spain, Portugal, and the Canary Islands, and afterwards to America: it was only after this last importation that it came into general use. The presence of cane-sugar in beet and other plants indigenous in Europe was first demonstrated, in 1747, by Marggraf, and its preparation on the large scale from beet was introduced by Achard. The chemical composition of cane-sugar was established by Gay-Lussac and Thénard.

Preparation.—Cane-sugar has not yet been formed artificially. It is prepared almost exclusively from the juice of the sugar-cane, and of field-beet or mangold-wurzel; smaller quantities are obtained from the sorgho and the sugar-maple.

1. From the Sugar-cane.—The ripe canes cut close to the ground and stripped of their leaves are crushed between rollers, and the expressed juice, which is apt to run quickly into fermentation by the action of the albuminous matters which it contains, is *defecated* by heating it in a copper boiler to about 60° C. (140° F.), with a small quantity of lime. The impurities then form a scum, which is removed as fast as it collects. The juice, when sufficiently clarified, is rapidly concentrated to about 23° of the hydrometer, then passed through cloth filters and evaporated to a very thick syrup, which is run into shallow vessels to accelerate cooling, then poured into vessels having their bottoms pierced with holes which are kept plugged. The syrup, after being left at rest for some hours, is agitated to promote the crystallisation of the sugar; and as soon as it has set into a solid mass, the plugs are removed, to allow the still remaining liquid to run off, and the syrup is again boiled till it no longer yields any crystals. The last mother-liquors, which are thick, brown, and refuse to crystallise, are called molasses or treacle, and are used chiefly for the preparation of rum.

The solid sugar, obtained as above, is sent to Europe under the name of raw sugar, or Muscovado sugar. It is a yellowish granular powder, still impregnated with treacle, and often contaminated with foreign substances, which impart to it a more or less disagreeable taste: hence it requires refining.

The formation of molasses is entirely due to the conversion of the cane-sugar into uncrystallisable sugar by the heat to which the juice is subjected; the fresh juice of sound canes contains nothing but crystallisable sugar. Great improvements have recently been effected in the methods of boiling down syrups, especially by the use of vacuum-pans, whereby a beautiful crystallised product is obtained from the juice at the first evaporation, and the formation of molasses is greatly diminished.

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* For Literature see *Gmelin's Handbook*, xv. 237.

On the manufacture of sugar from the cane, see *Ure's Dict. of Arts*, &c., iii. 802—816.—Manufacture of Maple-sugar, *ibid.* p. 826.

2. From **Beetroot.**—The roots of mangold-wurzel are reduced to a fine pulp, from which the juice is separated, either by pressure, after adding a quantity of water equal to 20 per cent. of the weight of the root; or by lixiviating it with cold water; or, finally, by subjecting it in perforated cylinders to the rotatory action of a centrifugal machine.—The juice is heated to 68° by hot steam, every 1000 quarts being mixed with a quantity of milk of lime prepared from 12 lbs. of lime, and the mixture is further heated to the boiling-point, whereby phosphate of calcium, albumin, albuminate of calcium, and other matters are separated, in the form of a dense white crust. The heating is interrupted as soon as the boiling juice begins to break through the crust, the clear liquid below is run off, and the muddy residue is submitted to pressure. The calcareous *thin syrup* thus obtained is treated with carbonic acid (from 0·6 to 0·8 per cent. lime, however, remains dissolved as sugar-lime); separated by subsidence and decantation from precipitated carbonate of calcium; filtered through bone-black, which removes a small quantity of sugar-lime; and evaporated to 20—22° Bm., either in open pans or in a vacuum-apparatus. The *thick syrup*, again filtered through bone-black, and evaporated in vacuo at about 22" barometric pressure, till it becomes thick enough to draw out into threads, yields, after cooling and standing, crystals of cane-sugar; and the mother-liquor, when further evaporated, yields a second and third crop, till nothing remains but uncrystallisable molasses. The last very dark-coloured crop of crystals is moistened with water, and freed from adhering molasses by means of the centrifugal machine. The mixture of all the successive crops of crystals thus obtained constitutes raw beet-sugar. (For details, see *Handw. d. Chem.* ix. 1101.)

Refining.—To obtain pure, colourless, crystallised sugar from raw sugar, the latter, dissolved in about a third of its weight of water, is mixed with a small quantity of milk of lime, and heated to the boiling-point; and the juice is decanted from the impurities, which separate in the form of a crust, then filtered through bone-charcoal, and evaporated in a vacuum pan. The strongly concentrated juice is made to crystallise by moderating the heat and running in small quantities of unthickened juice, whereupon a magma of sugar-crystals immediately forms. To give them the requisite hardness, heat is again applied, the crystalline magma is left to drain in the sugarloaf moulds, and the formation of small uniform crystals is promoted by stirring and breaking up the crust which forms on the surface. When the crystallisation is complete, the apex of the mould, which has previously been closed, is opened, to allow the syrup to drain off, and that which remains adhering to the crystals is displaced by pouring in pure sugar-syrup. By due desiccation, the *loaf-sugar* or *refined sugar* of commerce is obtained. (*Ure's Dict. of Arts*, &c. iii. 802.)

Formerly the clarification of the syrup was effected by adding a certain quantity of the serum of bullock's blood; on heating the syrup, the albumin of the serum became coagulated and rose to the surface, carrying with it the greater part of the impurities.

Preparation on the small scale.—The sacchariferous portion of a plant, after being dried and pulverised, is boiled with 2 pts. of strong alcohol, and the filtrate is left to cool; it then, after some time, deposits crystals of sugar. (**Marggraf.**)

From **fruits**, likewise containing uncrystallisable (inverted) sugar, cane-sugar may be extracted by filtering the expressed juice (after adding an equal volume of alcohol, if necessary, to prevent alteration), then saturating it with slaked lime, and filtering. The filtrate heated to the boiling-point, and again filtered at that temperature, leaves on the filter insoluble sugar-lime, which, after thorough washing with water, is to be decomposed by carbonic acid. The sugar-solution is then evaporated to a syrup, decolorised with animal charcoal, mixed with alcohol till it becomes turbid, and left to crystallise. The insoluble sugar-lime produced at the boiling heat does not contain more than $\frac{2}{3}$ of the total quantity of sugar present: hence the treatment with lime must be repeated. If the decomposition of the sugar-lime by carbonic acid yields very turbid liquids, they must be precipitated with basic acetate of lead, and the filtrate treated with sulphydric acid. (**Buignet.**)

Properties.—Cane-sugar separates from its solutions by slow evaporation in large crystals (sugar-candy), having the form of monoclinic prisms, generally with hemihedral faces. Axes $a : b : c = 0·7952 : 1 : 0·7$. Angle of axes b, $c = 76° 44'$; $\infty P : \infty P$ (orthod.) $= 101° 30'$; $+ P\infty : + P\infty$ (clinod.) $= 98° 50'$; $+ P\infty : c = 64° 12'$.—Ordinary combinations, $\infty P . oP . \infty P\infty$ (*fig.* 780), and $\infty P . oP . \infty P\infty . + P\infty . [P\infty]$ (*fig.* 781). By the cooling of hot saturated solutions, the sugar is obtained or masses of smaller crystals having the same form (loaf-sugar). The crystals exhibit phosphorescence when broken, also when a strong electric discharge is passed through them. Specific gravity = 1·606.

Fig. 780.

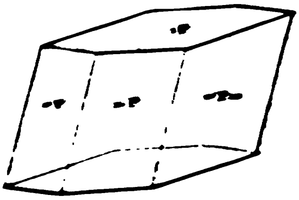
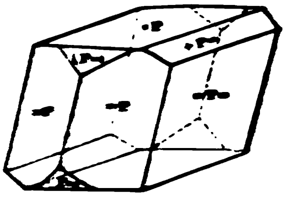


Fig. 781.



Cane-sugar is very soluble in water, dissolving in a third of its weight of cold, and still more easily in hot water: concentrated solutions are syrupy. It is insoluble in ether and in cold absolute alcohol; boiling alcohol dissolves about 1¼ per cent. of it; aqueous alcohol dissolves it much more readily.

Percentage of Cane-sugar in Aqueous Solutions of different Densities.

(Extracted from the Tables of Balling and Brix.)

Cane-sugar per cent.	Specific gravity at 17·5°.	Cane-sugar per cent.	Specific gravity at 17·5°.
1	1·0040	55	1·2610
5	1·0200	60	1·2900
10	1·0404	65	1·3190
15	1·0614	70	1·3507
20	1·0832	75	1·3824
25	1·1059	80	1·4159
30	1·1295	85	1·4499
35	1·1540	90	1·4849
40	1·1794	95	1·5209
45	1·2057	99	1·5594
50	1·2165		

The aqueous solution of cane-sugar turns the plane of a polarised ray to the right, for the transition-tint, $[\alpha]_j = +73·8°$. The rotatory power varies but little with changes of temperature.

Cane-sugar melts at 160° to a clear liquid, and solidifies on cooling to a transparent amorphous mass, commonly called barley-sugar, which gradually becomes opaque and crystalline.

Decompositions.—1. Cane-sugar heated a little above 160°, is converted, without loss of weight, into a mixture of *dextrose* and *levulosan* (ii. 864):

$$C^{12}H^{22}O^{11} = C^6H^{12}O^6 + C^6H^{10}O^5.$$

At a higher temperature, water is given off, the dextrose being probably converted into glucosan (ii. 854), afterwards at about 210°, more water is given off and caramel remains (1). At a still higher temperature, an inflammable gaseous mixture is given off, consisting of carbonic oxide, marsh-gas, and carbonic anhydride; a distillate is obtained, consisting of brown oils, acetic acid, acetone, and aldehyde; and a considerable quantity of charcoal remains behind. The brown oils contain a small quantity of furfurol (ii. 750), and a bitter substance called assamar (i. 418). (For further details respecting these products, see Gm. xv. 248.)

2. By prolonged boiling with *water*, cane-sugar is converted into a mixture of dextrose and lævulose, called inverted sugar (ii. 863), because the rotatory power of the lævulose is greater than that of the dextrose:

$$\underset{\text{Saccharose.}}{C^{12}H^{22}O^{11}} + H^2O = \underset{\text{Dextrose.}}{C^6H^{12}O^6} + \underset{\text{Lævulose.}}{C^6H^{12}O^6}.$$

This transformation is accelerated by the presence of acids, and apparently also of certain salts. Very dilute acids convert the cane-sugar into inverted sugar, slowly in the cold, very quickly when heated. Different acids act with various degrees of rapidity—mineral more quickly than organic acids, sulphuric acid most quickly of all. When sugar is boiled even with very dilute acids, especially if the boiling be long-continued, a number of brown amorphous products are formed, called ulmin, ulmic acid, &c. (Gm. xv. 254); if the air has access to the liquid, formic acid is likewise produced.—Concentrated hydrochloric acid decomposes sugar very quickly.

Strong sulphuric acid decomposes dry sugar when heated, and a concentrated solution, even at ordinary temperatures, with copious evolution of sulphurous anhydride and formation of a large quantity of black carbonaceous matter. By this reaction cane-sugar may be distinguished from glucose (ii. 859, 864).

3. Cane-sugar is very easily oxidised. It reduces *silver-* and *mercury-salts* when heated with them, and precipitates *gold* from the chloride. Pure *cupric hydrate* is but slowly reduced by it, even at the boiling heat; in presence of alkali, however, a blue solution is formed, and on boiling the liquid cuprous oxide is precipitated. An alkaline solution of *cupric tartrate* is very slowly reduced by cane-sugar.—Cane-sugar takes fire when triturated with 8 pts. *peroxide of lead*, and forms with *chlorate of potassium* a mixture which detonates on percussion, and burns vividly when a drop of oil of vitriol is let fall upon it. Cane-sugar, distilled with a mixture of *sulphuric acid* and *manganic peroxide*, yields formic acid. Heated with *dilute nitric acid*, it yields saccharic and oxalic acids. 1 pt. sugar mixed with 3 pts. nitric acid of specific gravity 1·25 to 1·30, and heated to 50°, is wholly converted into saccharic acid:

$$C^{12}H^{22}O^{11} + O^6 = 2C^6H^{10}O^8 + H^2O.$$

At the boiling heat, the product consists chiefly of oxalic acid. Very strong nitric acid, or a mixture of strong nitric and sulphuric acids, converts sugar into nitrosaccharose, probably $C^{12}H^{18}(NO^2)^4O^{11}$. Sugar is likewise oxidised by *chloride of lime*, but the products have not been examined.

4. Cane-sugar does not turn brown when triturated with *alkalis*, a character by which it is distinguished from glucose: it combines with them, however, forming compounds called sucrates. By boiling with *potash-ley* it is decomposed, but much more slowly than the glucoses. When fused with *potassium-hydrate* containing water, it yields chiefly formic, acetic, and propionic acids; with dry potassium-hydrate it yields oxalic acid (Gottlieb, Ann. Ch. Pharm. lii. 122). Distilled with *soda-lime*, it yields small quantities of ethylene, tritylene, and amylene (Berthelot, Jahresb. 1857, p. 426); and, when distilled with *quicklime*, it gives off acetone, metacetone, &c. (Gottlieb.)

5. Dry *chlorine* does not attack sugar at ordinary temperatures; but at 100°, a brown substance is formed, partly soluble in water. On passing chlorine into sugar-water, hydrochloric acid is slowly formed, together with carbonic acid, a brown substance, and an uncrystallisable organic acid.—*Perchlorides* act upon sugar (and other carbohydrates) in the same manner as free chlorine, producing dark-coloured products. This reaction is applied by Maumené (Compt. rend. xxx. 314) to the detection of sugar and analogous substances in liquids. For this purpose a drop of the liquid is placed on a strip of white merino, previously steeped in a solution of stannic chloride and dried; and the strip is warmed over a hot coal or the flame of a lamp: the presence of any saccharine substance will then be indicated by the production of a black spot.

6. Sugar does not absorb *fluoride of boron* in the cold, but on applying heat, the gas is absorbed, and the sugar is blackened.

7. Cane-sugar is not directly *fermentable*, but when its dilute aqueous solution is mixed with yeast, and exposed to a warm atmosphere, it is first resolved into a mixture of dextrose and lævulose (p. 470), which then enter into fermentation, yielding alcohol and carbonic anhydride:

$$C^6H^{12}O^6 = 2C^2O^2 + 2C^2H^6O.$$

When equal weights of cane-sugar and glucose are dissolved in equal quantities of distilled water, and a very small quantity of yeast added to each, the glucose immediately begins to ferment, even at the mean temperature of summer (about 20°); but the cane-sugar remains unaltered for months, even at 30°—40°. To bring it to the fermenting state, it is necessary to add seven or eight times the original quantity of yeast (H. Rose, J. pr. Chem. xxiii. 393). The conversion of cane-sugar into inverted sugar is effected by the soluble ferment in yeast (analogous to diastase), and by the ferment contained in most fruits.

Estimation of Cane-sugar: Saccharimetry.—If the solution contains nothing but cane-sugar, the specific gravity is observed, and the percentage of sugar determined therefrom (*vid. inf.*). If other substances which affect the density are likewise present, the quantity of cane-sugar may be determined:

1. From the weight of carbonic anhydride formed in the vinous fermentation of the sugar, or from the quantity of alcohol thereby produced. According to older statements, 100 pts. cane-sugar yield (after deduction of 5·26 pts. water), 51·44 pts. carbonic anhydride and 53·80 absolute alcohol; according to Pasteur's direct determination, 49·12 pts. carbonic anhydride and 51·01 absolute alcohol, the remaining portion of the sugar being consumed in the formation of glycerin and succinic acid. See

ii. 628; also **Buignet's** description of the process. (Ann. Ch. Phys. [3], lxi. 239.)

2. From the weight of cuprous oxide which the sugar can reduce from potassio-cupric tartrate, or from the volume of a standard solution of that salt decomposed by the sugar. For this reaction, the cane-sugar must be previously heated with acids, to convert it into inverted sugar, which reduces the same quantity of cupric oxide as grape-sugar. (See GLUCOSE, ii. 863.)

3. *From the Rotatory Power of the Solution.*—If the solution contains only cane-sugar, or, at least, no other optically active substance, the amount of sugar may be calculated from the rotatory power in the manner described under LIGHT (iii. 673). Turbid or gummy solutions are mixed with $\frac{1}{10}$ their volume of isinglass-solution; then, after agitation, with 1½ vol. alcohol, whereupon the mixture, without being heated, coagulates, and yields a filtrate adapted for observation. Coloured solutions are decolorised by animal charcoal; but as this substance (according to some statements) takes up sugar, the first fourth of the liquid that runs through is rejected, and only the remainder used for the observation. If, in addition to cane-sugar, the solution contains grape-sugar, inverted sugar, or any other optically active substance, whose rotatary power is not altered by heating with acids, the amount of cane-sugar may be determined by observing the rotatory power of the solution, both before and after inversion, the temperature being likewise observed in the latter case. The first observation having been made, 100 c.c. of the solution are mixed with 10 c.c. fuming hydrochloric acid, the mixture heated to 68°, and kept at that temperature for a quarter of an hour. Since the rotatory power of the solution cooled to the original temperature (supposing the observation to have been made in a tube longer by one-tenth than the former), remains unaltered in so far as it was due to the glucose, whereas the cane-sugar has been replaced by inverted sugar, the amount of cane-sugar may be calculated from the rotatory power peculiar to this inverted sugar, as follows:—The rotatory power (a) observed before inversion was made up of the molecular rotatory power (c) of the cane-sugar (C), and that of the grape-sugar ($g\,G$): therefore

$$a = c\,C + g\,G.$$

The rotatory power (a') observed after inversion is, in like manner, made up of the unaltered rotatory power of the grape-sugar ($g\,G$), and that of the inverted sugar ($i\,C$); therefore:

$$a' = i\,C + g\,G.$$

Consequently the difference, $a - a'$, of the rotations observed before and after inversion, is equal to $c\,C - i\,C$:

$$a - a' = C(c - i).$$

or, finally:

$$C = \frac{a - a'}{c - i}$$

Suppose, for example, a sugar-solution before inversion turns the plane of polarisation 25·96° to the right, and after inversion, 5·80° to the right, at a temperature of 14°; then $a = 25{\cdot}96$ and $a' = 5{\cdot}80$. Now, the molecular rotatory power of cane-sugar (c) is 73·8°, and that of inverted sugar is 25° at the temperature of 15°: consequently,

$$C = \frac{25{\cdot}96 - 5{\cdot}80}{73{\cdot}8 + 27} \quad \text{or} \quad C = \frac{20{\cdot}16}{98{\cdot}8} = 0{\cdot}204\,;$$

which quantity, therefore, gives the number of parts by weight of cane-sugar contained in a unit of weight of the solution employed, or, when multiplied by 100, the percentage of cane-sugar in the solution.

Suppose another sugar-solution, before inversion, to turn the plane of polarisation 9·36° to the right, and after inversion 10·80° to the left (= −10·80° to the right): in this case, $a = 9{\cdot}36$; $a' = -10{\cdot}80$, $a - a' = 9{\cdot}36 + 10{\cdot}80 = 20{\cdot}16$, which number divided by 98·8 again gives 0·2, or 20 per cent. of cane-sugar in the solution.

If, in both cases, the nature of the second optically active substance present in addition to the cane-sugar is known, its quantity may be determined from the observations just described; if, on the other hand, its quantity is previously known, its nature may be determined. Thus, it might be inferred that grape-sugar was present, in the first case, besides the cane-sugar in the original solution, and inverted sugar in the second. This mode of proceeding, however, is admissible only when the deflection after inversion has been observed at a temperature for which the molecular rotatory power of the inverted sugar (which varies with the temperature) has been previously determined. (**Biot**, Compt. rend. xv. 523, 619, and 694 [3], xvii. 755.—**Clerget**, Ann. Ch. Phys. [3], xxvi. 175; Jahresb. 1849, p. 126.)

Compounds and Derivatives of Cane-sugar.

I. **With Acids.**—The compounds formed by the action of acids on cane-sugar may be divided into two groups:

a. Ethereal Compounds of Cane-sugar itself.—The only known compound belonging to this group is:

Nitrosaccharose, $C^{12}H^{18}(NO^2)^4O^{11}$?, produced by adding cane-sugar to a mixture of strong sulphuric and nitric acids. It is an amorphous mass, which detonates when struck. (Gm. xv.)

β. Ethereal compounds of the glucoses, produced from cane-sugar by the action of acids. To this class belong the saccharides obtained by heating cane-sugar with acetic, butyric, and stearic acid (ii. 855; v. 144).

II. **With Bases.** (Péligot, Ann. Ch. Pharm. xxx. 69, 92; lxxx. 342.—Stein, *ibid.* xxx. 82.—Soubeiran, *ibid.* xliii. 125, 227.—Berthelot, Jahresb. 1856, p. 635):

Potassium- and *Sodium-compounds* of cane-sugar, $C^{12}H^{21}KO^{11}$ and $C^{12}H^{21}NaO^{11}$, are formed, as gelatinous precipitates, on mixing an alcoholic solution of cane-sugar with potash- or soda-ley.

A *barium-compound*, $C^{12}H^{20}Ba''O^{11}.H^2O$ or $C^{12}H^{22}O^{11}.Ba''O$, is obtained, as a crystalline precipitate, on adding hydrate or sulphide of barium to an aqueous solution of sugar. It may be crystallised from boiling water, but is insoluble in alcohol.

Calcium-compounds.—Lime dissolves in sugar-water much more readily than in pure water. The solution has a bitter taste, and is completely but slowly precipitated by carbonic acid. There are three or four of these compounds, which may be approximately represented by the following formulæ:

(1.) $C^{12}H^{22}O^{11}.Ca''O$.
(2.) $2C^{12}H^{22}O^{11}.3Ca''O$ (?).
(3.) $C^{12}H^{22}O^{11}.2Ca''O.2H^2O$.
(4.) $C^{12}H^{22}O^{11}.3Ca''O$.

The constitution of these compounds is not exactly known; but a part, at least, of the calcium probably replaces hydrogen in the sugar.

The first compound, **monocalcic sucrate**, is soluble in water, and is obtained as a white precipitate on adding alcohol to a solution of calcic hydrate in sugar-water, not containing too much lime.—The compound (2) is formed when sugar-water is boiled with excess of calcic hydrate, and the filtrate is evaporated: it is probably a mixture of (1) and (3).—The compound (3) is precipitated by alcohol, from the liquid obtained by digesting sugar-water with excess of calcic hydrate.—The compound (4) is slightly soluble in water, and separates, on heating a cold-digested solution of calcic hydrate in sugar-water, as an amorphous mass: hence solutions of lime in sugar-water usually solidify to a pasty mass when boiled.

Magnesia and *lead-oxide* are likewise dissolved by sugar-water. A crystalline **lead-compound**, $C^{12}H^{18}Pb^2O^{11}$, is obtained by boiling sugar-water with litharge, and leaving the filtrate to cool; by mixing sugar-water with neutral lead-acetate and ammonia; or by precipitating neutral lead-acetate with a solution of sugar-lime.

III. **With Salts.**—*a.* With *Chloride of Sodium*, $C^{12}H^{22}O^{11}.NaCl$.—This compound separates, in small deliquescent crystals, from a mixed solution of common salt and sugar. (Péligot, Ann. Ch. Pharm. xxx. 71.)

β. With *Borax*, $3C^{12}H^{22}O^{11}.(Na^2O.2B^2O^3).5H^2O$.—Borax dissolves in sugar-water more freely than in pure water, and the solution, when evaporated or precipitated with alcohol, yields this compound.

Parasaccharose. This is an isomer of cane-sugar, produced, according to Jodin (Compt. rend. liii. 1252; lv. 720: Jahresb. 1861, p. 722; 1862, p. 473), by spontaneous fermentation. An aqueous solution of cane-sugar containing phosphate of ammonium left to itself in summer (between June 15 and September 15, 1861), yielded, under circumstances not further specified, a crystallisable sugar isomeric with saccharose, together with an amorphous sugar having the composition of a glucose, both dextrorotatory. Parasaccharose, $C^{12}H^{22}O^{11}$, is very soluble in water, nearly insoluble in alcohol of 90 per cent. Specific rotatory power at 10° = + 108°, appearing to increase a little with rise of temperature. It does not melt at 100°, but becomes coloured, and appears to decompose. It reduces an alkaline cupric solution, but only half as strongly as dextrose (1 at. parasaccharose = 5 at. CuO; 1 at. dextrose = 10 at. CuO). It is not perceptibly altered by dilute sulphuric acid, even at 100°; hydrochloric acid weakens its rotatory power, turns the solution brown, and heightens its reducing power for cupric oxide.

Paraglucose. This is the amorphous dextrorotatory sugar produced, together with parasaccharose, as above described. When dried at 15°, it has the composition $C^6H^{12}O^6.H^2O$. It is hygroscopic, gives off half its water of crystallisation at 50° and the whole at 100°, melting, and turning brown at the same time. Its specific rotatory power is about + 40°. It reduces alkaline cupric solutions less strongly than glucose, and about as strongly as milk-sugar (1 at. paraglucose = 7 at. CuO). It is not perceptibly altered by dilute acids, even with aid of heat, excepting that its rotatory power is diminished to about + 32°, and its reducing action is increased to about that of glucose. (Jodin.)

SUGAR, INVERTED. The mixture of dextrose and lævulose in equal numbers of atoms, produced by the transformation of cane-sugar under the influence of acids (ii. 863).

SUGAR OF FRUITS. This term is applied especially to the uncrystallisable mixtures of dextrose and lævulose contained in many fruits. Some fruits, however, contain crystallisable sugars—viz., dextrose, saccharose, or the two together (p. 468).

SUGAR OF LEAD. Neutral plumbic acetate (i. 16).

SUGAR-CANDY. Cane-sugar crystallised by slow evaporation.

SUGAR-CANE. *Saccharum officinarum.*—This important grass, which yields by far the larger quantity of the sugar at present consumed, thrives only in hot climates. It has been known in India and China from very early times, and its cultivation appears to have been introduced into the West Indies in the fifteenth century. There are several varieties of the cane. The longest known is the creole or common sugar-cane, which grows freely in every region between the tropics on a moist soil, and even at an elevation of 3,000 feet above the sea-level. A superior variety is the Otaheitan cane, which is stronger, taller, quicker in growth, and much more productive in sugar. The cane thrives best on a light rich soil, especially on one manured with nitrogenous refuse.

The fresh cane contains, according to two analyses by Péligot and Dupuy:

Water	72·1	72·0
Sugar	18·0	17·8
Woody fibre	9·9	9·8
Salts		0·4
	100·0	100·0

The creole cane of Havanna has been analysed by Casaseca (Ann. Ch. Phys. [3] xxv. 321), with the following results:

	Cane entire.	Cane peeled.	Rind.
Water	77·0	77·8	69·5
Sugar and other soluble substances	12·0	16·2	11·5
Woody substance	11·0	6·0	19·0
	100·0	100·0	100·0

Casaseca finds that the juice is richer in sugar at the base of the cane, and becomes gradually poorer towards the top.

The specific gravity of cane-juice varies from 1·046 to 1·110, but is generally from 1·070 to 1·090, or from 10° to 13° Bm. It is opaque, frothy, and of a yellowish-green colour. On boiling, a green scum rises, and the liquid remains of a pale-yellow colour. The green scum (dried) consists, according to Arequin, of 50 per cent. of a peculiar wax called cerosie, 10·0 green matter, 22·7 albumin and woody fibre, 3·3 calcic phosphate, and 14·0 silica. The pure juice contains 81·0 per cent. water, 18·20 sugar, 0·45 organic matter precipitated by lead-salts, and 0·35 saline matter.

The ash of the cane contains, according to Stenhouse:

SiO^2.	P^2O^5.	SO^3.	CaO.	MgO.	K^2O.	Na^2O.	KCl.	NaCl.	
46·46	8·23	4·65	8·91	4·50	10·63	. .	7·41	9·21	= 100
41·37	4·59	10·93	9·11	6·92	15·99	. .	8·96	2·18	= 100
46·48	8·16	7·52	5·78	15·61	11·93	0·57	. .	3·95	= 100
50·00	6·56	6·40	5·09	13·01	13·69	1·33	. .	3·92	= 100

The proportion of salts in the juice varies considerably with the soil on which the canes are grown. (*Ure's Dictionary of Arts*, &c. iii. 808.)

SUGAR-CANE, CHINESE. See SORGHO (p. 354).

SUGAR-MAPLE. *Acer saccharinum.*—The stem of this tree, which grows wild in many parts of North America, yields a sugar identical with that of the cane. To obtain it, the trees are bored in the early spring, and the juice, collected in vessels suspended beneath, is boiled as quickly as possible to prevent fermentation. As soon as the syrup flows from the stirrer, in thick drops of the consistence of honey, it is strained through a wooden sieve, then left to stand for eight or ten hours, clarified with a little white of egg, boiled, skimmed, and quickly evaporated to the crystallising-point.

SULPHACETAMIDE. This name is applied by E. Schulze (Zeitschr. Ch. Pharm. 1865, p. 73), to the compound $\left.\begin{matrix}(C^4H^4S''O^2)''\\ H^4\end{matrix}\right\}N^2$, produced by the action of ammonium-sulphide on chloracetamide, the corresponding acid, $\left.\begin{matrix}(C^4H^4S''O^2)''\\ H^2\end{matrix}\right\}O^2$, being called sulphacetic acid (*monosulphacetsäure*); but as this latter name has long been appropriated to the acid, $C^2H^4O^2.SO^3$, produced by the action of sulphuric anhydride on acetic acid, it is better to designate Schulze's acid as thiodiacetic acid, and the amide as thiodiacetyl-diamide, a name which expresses that the radicle, $C^4H^4SO^2$, contained in it is derived from a double molecule of acetyl, $C^4H^6O^2$, by the substitution of S'' for H^2. (See THIODIACETIC ACID.)

SULPHACETIC ACID. $C^2H^4SO^5 = C^2H^4O^2.SO^3$ $\left.\begin{matrix}(C^2H^2SO^3)''\\ H^2\end{matrix}\right\}O^2 = \left.\begin{matrix}(C^2H^2O)''\\ (SO)''\\ H^2\end{matrix}\right\}O^2$. *Glycolyl-sulphurous acid. Sulpho-essigsäure. Essigschwefsäure.* (Melsens, Ann. Ch. Phys. [3], v. 392; x. 370.—Buckton and Hofmann, Chem. Soc. Qu. J. ix. 247.)—This acid is produced: 1. By the action of sulphuric anhydride on acetic acid. Glacial acetic acid is gradually saturated with sulphuric anhydride, the liquid being cooled after each addition; the mixture is diluted with water, and neutralised with lead-carbonate; the filtered solution is evaporated to the crystallising-point; and from the lead-salt thus obtained, the sulphacetic acid is separated by sulphydric acid (Melsens).—2. By the action of fuming sulphuric acid on acetamide or acetonitrile (Buckton and Hofmann):

$$\underset{\text{Acetonitrile.}}{C^2H^3N} + H^2O + 2H^2SO^4 = \underset{\text{Sulphacetic acid.}}{C^2H^4SO^5} + NH^4.H.SO^4.$$

This is the reaction which chiefly takes place when the materials are gradually mixed, and the mixture is cooled from time to time; if, on the other hand, the temperature is allowed to rise, carbonic anhydride is evolved, and disulphometholic acid is produced, instead of sulphacetic acid, according to the equation:

$$C^2H^3N + 3H^2SO^4 = CH^4S^2O^6 + NH^4.H.SO^4 + CO^2.$$

Sulphacetic acid forms deliquescent prisms, which melt at 62°, and decompose at 200°. It is very soluble in water, forming an acid solution, which is not decomposed by boiling (Melsens). The acid, heated with fuming sulphuric acid or sulphuric anhydride, is converted into disulphometholic acid. (Buckton and Hofmann.)

Sulphacetic acid is dibasic. Its salts are all soluble in water, the barium-salt being the least soluble; they are insoluble in alcohol. When heated with strong sulphuric acid, they give off carbonic and sulphurous anhydrides.

Sulphacetate of Potassium, $C^2H^2K^2SO^5.H^2O$, is deposited from a hot solution on cooling, in small, hard, easily pulverisable crystals.—The *barium-salt*, when pure, forms small opaque crystals, $C^2H^2Ba''SO^5.\frac{3}{2}H^2O$, which give off a third of their water at 100°, and the whole at 250°.—The *lead-salt*, $C^2H^2Pb''SO^5$, is deposited, sometimes in radiate groups of short transparent needles, sometimes in opaque nodules, which do not retain any water at 120°.—The *silver-salt*, $C^2H^2Ag^2SO^5$, is deposited from a boiling saturated solution in small flat prisms, bevelled at the ends. In the mother-liquor obtained in the preparation of this salt by saturating the acid with silver-oxide, Melsens found a salt containing $CH^2Ag^2S^2O^6$, doubtless disulphometholate of silver.

SULPHACETYLENIC ACID. *Acetschwefsäure.* $C^2H^4SO^5 = \left.\begin{matrix}(C^2H^2)''\\ (SO^2)''\\ H^2\end{matrix}\right\}O^2$. (Kämmerer and Carius, Ann. Ch. Pharm. cxxxi. 165; Jahresb. 1864, p. 326.)—This acid, isomeric with sulphacetic acid, is produced by heating 1 at. argentic sulphate (mixed with glass powder) with 2 at. chloride of acetyl to 120°, and treating the product with water:

$$\underset{\text{Argentic sulphate.}}{\left.\begin{matrix}(SO^2)''\\ Ag^2\end{matrix}\right\}O^2} + 2(C^2H^3O.Cl) = 2AgCl + \underset{\text{Acetosulphuric anhydride.}}{\left.\begin{matrix}(SO^2)''\\ (C^2H^3O)^2\end{matrix}\right\}O^2} \left[\text{or, } \left.\begin{matrix}(SO^2)''\\ (C^2H^2O)''\\ (C^2H^3O).H\end{matrix}\right\}O^2\right].$$

$$\underset{\text{Acetosulphuric anhydride.}}{\left.\begin{matrix}(SO^2)''\\ (C^2H^2)''\\ (C^2H^3O).H\end{matrix}\right\}O^2} + H^2O = \underset{\text{Sulphacetylenic acid.}}{\left.\begin{matrix}(SO^2)''\\ (C^2H^2)''\\ H^2\end{matrix}\right\}O^2} + \underset{\text{Acetic acid.}}{\left.\begin{matrix}C^2H^3O\\ H\end{matrix}\right\}O}.$$

By neutralising the resulting solution with lead-carbonate, decomposing the filtrate with sulphydric acid, and evaporating in a vacuum, the sulphacetylenic acid is obtained as a viscid liquid, which gradually decomposes into sulphuric and acetic acids. With pentachloride of phosphorus it first yields the chloride, $C^2H^2SO^3Cl^2$ (which boils at 150°, and is resolved by water into hydrochloric and sulphacetylenic acid), and then, as final products, chloride of chloracetyl * and chloride of sulphuryl:

$$\underset{\substack{\text{Sulphacety-}\\\text{lenic acid.}}}{\left.\begin{matrix}SO^2\\C^2H^2\\H^2\end{matrix}\right\}O^4} + 2PCl^5 = \underset{\substack{\text{Sulphacetyle-}\\\text{nic chloride.}}}{\begin{matrix}SO^2\\C^2H^2\end{matrix}\left\{\begin{matrix}O\\Cl^2\end{matrix}\right.} + 2POCl^3 + 2HCl.$$

$$\underset{\substack{\text{Sulphacety-}\\\text{lenic chloride.}}}{\begin{matrix}SO^2\\C^2H^2\end{matrix}\left\{\begin{matrix}O\\Cl^2\end{matrix}\right.} + PCl^5 = \underset{\substack{\text{Chloride of}\\\text{sulphuryl.}}}{SO^2Cl^2} + \underset{\substack{\text{Chloride of}\\\text{chloracetyl.}}}{C^2H^2ClO.Cl} + PCl^3.$$

By this behaviour, according to Kämmerer and Carius, sulphacetylenic acid is distinguished from sulphacetic acid: they do not, however, state distinctly in what manner the latter acid reacts with pentachloride of phosphorus. (Compare SULPHOBENZYLENIC ACID.)

Sulphacetylenic acid is dibasic.—The *potassium-salt*, $C^2H^2K^2SO^5.H^2O$, is easily soluble in water, and crystallises in needles and short prisms.—The *barium-salt*, $C^2H^2Ba''SO^5.H^2O$, is somewhat sparingly soluble, and crystallises in hard right rhombic prisms.

SULPHAMETHYLANE. Syn. with METHYLIC SULPHAMATE (p. 477).

SULPHAMIC ACID. $NH^3SO^3 = \left.\begin{matrix}NH^2(SO^2)''\\H\end{matrix}\right\}O = \left.\begin{matrix}H^2\\(SO^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}.$—This compound, the amic acid of sulphuric acid, is not known in the free state, that is to say, as a hydrogen-salt; but the so-called anhydrous sulphate of ammonia, called "sulphatammon" by H. Rose, "sulphamide" by Dumas, is probably its neutral ammonium-salt.

Neutral Sulphamate of Ammonium, $N^2H^6SO^3 = 2NH^3.SO^3 = \left.\begin{matrix}H^2\\(SO^2)''\\NH^4\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}.$ (H. Rose, Pogg. Ann. xxxii. 81; xlvii. 471; xlix. 183.)—This salt is produced when dry ammonia-gas is passed over a thin layer of sulphuric anhydride, care being taken to renew the surface frequently by scraping, as otherwise the lower portions will not be attacked by the ammonia. The product is a white crystalline powder, having a bitter taste, and perfectly neutral if it does not contain either free ammonia or free sulphuric anhydride. It is permanent in the air, dissolves without sensible decomposition in 9 pts. of water, and is insoluble in alcohol. The dry salt is decomposed by heat, giving off ammonia and sulphurous anhydride, and leaving a residue of sulphate of ammonium. Platinic chloride added to the aqueous solution, throws down half the nitrogen as ammonium-chloroplatinate. The caustic alkalis and their carbonates decompose the salt, even in the cold, with evolution of ammonia. The aqueous solution is clouded by chloride of barium, the precipitate gradually increasing on standing, and especially if the liquid be heated; but the precipitation is never complete, not more than half the sulphur being separated as sulphate of barium.

The aqueous solution, evaporated over oil of vitriol in a vacuum, yields transparent, colourless, hemihedral crystals, belonging to the quadratic system. These crystals have exactly the same composition as the original pulverulent salt, and were therefore designated by Rose as parasulphatammon. They doubtless consist of the pure neutral sulphamate of ammonium, quite free from adhering sulphuric acid. They dissolve in water more easily than the original salt, forming a perfectly neutral solution, which reacts in the same manner with platinic chloride, but gives no precipitate with chloride of barium, except after prolonged boiling.

The mother-liquor of parasulphatammon yields, by further evaporation, a hydrated salt, $2N^2H^6SO^3.H^2O$, in indistinct deliquescent crystals, very soluble in water, and exhibiting signs of decomposition, as their solution is faintly acid, and immediately gives a slight precipitate with chloride of barium.

Acid Sulphamate of Ammonium, $N^2H^6SO^3.NH^3SO^3$.—Produced, simultaneously with the neutral salt, as a hard vitreous mass, which deliquesces rapidly in the air, and dissolves in water with a hissing noise (H. Rose). According to Woronin (Rép. Chim. pure, ii. 452), an aqueous solution of the neutral sulphamate left to evaporate in the air, yields an abundant crystallisation of the acid sulphamate. Its solution is not precipitated by chloride of barium, excepting after neutralisatien with ammonia (*infra*).

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* The chloride of chloracetyl is converted, by excess of phosphoric pentachloride, into a colourless liquid, probably $C^2H^2Cl^4$, not decomposible by potash-ley, but resolved by water at 150° into hydrochloric and monochloracetic acid.

Sulphamate of Barium.—When a solution of the neutral ammonium-salt is mixed with an exactly equivalent quantity of baryta-water, ammonia is evolved, and the filtered liquid yields crystals of an easily soluble barium-salt.

The precipitate formed by chloride of barium in a solution of the acid ammonium-salt mixed with ammonia, consists of a *basic sulphamate of barium*, which, when treated with the proper quantity of sulphuric acid, yields a precipitate of barium-sulphate and a solution of *neutral barium-sulphamate*, $N^2H^4Ba''S^2O^6 = \left.\begin{matrix}H^4\\(SO^2)^2\\Ba''\end{matrix}\right\}\begin{matrix}N^2\\O^2\end{matrix}$. This salt forms well-developed crystals, sparingly soluble in cold water, and is decomposed by hot water, with formation of barium-sulphate. (Woronin.)

Sulphamate of Potassium, obtained by decomposing the barium-salt with sulphate of potassium, forms small transparent crystals; on addition of barium-chloride and ammonia to its solution, it is converted into basic sulphamate of barium. (Woronin.)

SULPHAMIC ETHERS. *Methylic Sulphamate*, or *Sulphamethylane*, $CH^5NSO^3 = \left.\begin{matrix}H^2\\(SO^2)''\\CH^3\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$.—This compound, which has the composition of anhydrosulphate of methylamine, is formed by dissolving methylic sulphate in aqueous ammonia, and crystallises, by evaporation in a vacuum, in large, very deliquescent crystals.

Phenylsulphamic or **Sulphanilic Acid,** $C^6H^7NSO^3 = \left.\begin{matrix}C^6H^5.H\\(SO^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$, or $\left.\begin{matrix}NH(C^6H^5)(SO^2)''\\H\end{matrix}\right\}O$. (Gerhardt, J. Pharm. [3], x. 5.—Buckton and Hofmann, Chem. Soc. Qu. J. ix. 259.—R. Schmitt, Ann. Ch. Pharm. cxx. 129.)—This acid, isomeric with amidosulphobenzolic acid, $C^6H^5(NH^2)SO^3$, is formed by the action of sulphuric acid on aniline, or on oxanilide (phenyloxamide):

$$\underset{\text{Oxanilide.}}{C^2H^2(C^6H^5)^2N^2O^2} + 2H^2SO^4 = \underset{\text{Sulphanilic acid.}}{2C^6H^7NSO^3} + CO + CO^2 + H^2O.$$

Preparation.—1. From the mixture of oxanilide and formanilide obtained by heating oxalate of aniline (iv. 427). This mixture is made up into a thick paste with strong sulphuric acid, and gently heated as long as effervescence continues; then exposed to moist air in a shallow dish, till it solidifies to a crystalline pulp of sulphanilic acid, which may be purified by washing with cold, and recrystallising from boiling water (Gerhardt).—2. By dissolving aniline in a slight excess of sulphuric acid, evaporating to dryness, and heating the residue with constant agitation, as long as vapours of aniline (?) continue to escape. The product is purified as before (Gerhardt).—Schmitt mixes 1 pt. of aniline by drops with 2 pts. of fuming sulphuric acid in a porcelain dish, heats the brown syrupy liquid till it becomes dark-brown and gives off a large quantity of sulphurous anhydride; and pours the thick syrup when cold into cold water: the sulphanilic acid then separates as a black crystalline mass, which may be purified by repeated recrystallisation from hot water, with addition of animal charcoal. This, according to Schmitt, is the best mode of preparing sulphanilic acid: Gerhardt, on the other hand, preferred the preparation from oxanilide.

β-Sulphanilic Acid.—Laurent (Compt. rend. xxxi. 538) obtained an acid, having the composition of sulphanilic acid, by treating nitrosulphobenzoate of ammonium with sulphydric acid. Kolbe (Ann. Ch. Pharm. cxiii. 318) suggested that the acid thus obtained was not identical, but only isomeric, with Gerhardt's sulphanilic acid; and this supposition has been corroborated by Schmitt, who has pointed out several differences in the characters of the two acids and their salts (*infra*). Kekulé (*Lehrbuch*, ii. 605) regards it as probable that Laurent's acid is the true phenylsulphamic or sulphanilic acid, and that the acid produced by the action of sulphuric acid on aniline or oxanilide is amidosulphobenzolic acid. Till this question is satisfactorily decided, it may be convenient to designate Laurent's acid as β-sulphanilic acid. Schmitt prepares this acid by mixing 1 pt. of nitrobenzol with 5 or 6 pts. of fuming sulphuric acid, leaving the mixture for several days in a warm place, and shaking it frequently till all the nitrobenzol has disappeared. The viscid mass is then neutralised with carbonate of lead; the colourless solution of plumbic nitrosulphobenzolate, obtained by boiling and filtering the liquid, is decomposed by sulphydric acid; the liquid, filtered from lead-sulphide, is neutralised with carbonate of barium; and the resulting barium-salt (which separates in warty crystals) is dissolved in a large quantity of water, and mixed with a large excess of baryta. Sulphydric acid gas is then passed into the liquid, till the taste of the nitro-acid is completely removed; and the liquid, filtered from hyposulphite of barium, is again treated with sulphydric acid. The filtered solution of the barium-salt, treated with an exactly equivalent quantity of sulphuric acid, yields the aqueous β-sulphanilic acid, which may be obtained in crystals by evaporation.

Properties.—Sulphanilic acid (from aniline or oxanilide) crystallises from hot water in shining rhombic plates, containing, according to Schmitt, $C^6H^7NSO^3.H^2O$. It is slightly soluble in cold water, 1 pt. [of the anhydrous or hydrated acid?] dissolving in 128 pts. of ice-cold water, and in 112 pts. at 15° (Schmitt); still less soluble in alcohol (Gerhardt), insoluble in alcohol and in ether (Schmitt). From a concentrated solution of a sulphanilate, it is precipitated by acids in slender needles.

The crystals give off their water partially on exposure to the air, completely at 100°; the effloresced acid, if exposed for some time to this temperature, assumes a brownish colour, but may be heated to 220° without decomposing. At higher temperatures it decomposes, leaving a carbonaceous residue, and giving off sulphurous anhydride; also, if distilled in a retort, sulphite of aniline, which crystallises in the receiver. Heated with a solid caustic alkali, or with potash-lime, it gives off aniline and leaves an alkaline sulphate. Heated with strong *nitric acid*, it evolves a large quantity of gas, and forms a deep red liquid, but no crystals (Gerhardt). Its aqueous solution is coloured red-brown, without precipitation, by *chromic acid*. *Chlorine-water* colours it pale-crimson, gradually changing to red-brown (Gerhardt). According to Schmitt, the aqueous solution is not altered either by chlorine or by iodine. *Bromine*, added even to a dilute solution of the acid, renders it milky, and throws down after a while a white curdy precipitate (Gerhardt). From a hot solution it throws down white interlaced needles of tribromaniline:

$$\underset{\text{Sulphanilic acid.}}{C^6H^7NSO^3} + Br^6 = \underset{\text{Tribromaniline.}}{C^6H^4Br^3N} + SO^3 + 3HBr.$$

If only 4 at. bromine be added, dibromosulphanilic acid, $C^6H^5Br^2NSO^3$, is likewise formed, and remains dissolved (Schmitt, p. 479).—With *nitrous acid*, it forms diazosulphobenzolic acid (Schmitt):

$$\underset{\text{Sulphanilic acid.}}{2C^6H^7NSO^3} + N^2O^3 = \underset{\text{Diazosulphobenzolic-acid.}}{2C^6H^4N^2SO^3} + 3H^2O.$$

β-Sulphanilic acid crystallises from its aqueous solution by evaporation in long pointed crystals, which contain $2C^6H^7NSO^3.3H^2O$, give off their water partially at ordinary temperatures, completely at 100°, and becoming white and opaque. It is insoluble in ether and alcohol, easily soluble in hot water. With *bromine* it behaves somewhat differently from sulphanilic acid, inasmuch as, though its concentrated solutions are rendered turbid by bromine, the liquid filtered therefrom does not give any precipitate with chloride of barium, as is the case with that obtained in like manner from sulphanilic acid (p. 479).

Sulphanilates.—Sulphanilic acid is a strong acid, and decomposes carbonates with effervescence. Its salts are soluble and crystallisable; their solutions give, with chromic acid and bromine-water, the same reactions as the free acid. The β-sulphanilates differ from the sulphanilates in crystalline form. (Schmitt.)

Sulphanilate of Ammonium, $C^6H^6(NH^4)NSO^3$, is very soluble, and crystallises by spontaneous evaporation, in shining rectangular plates.—The *aniline-salt* is very soluble.—The *barium-salt* forms rectangular prisms, moderately soluble in water.—The *cupric salt*, $C^{12}H^{12}Cu''N^2S^2O^6.4H^2O$, forms small truncated prisms of a very dark green colour, which retain their water at 100°.—The *silver-salt* crystallises in shining scales.—The *sodium-salt*, $C^6H^6NaNSO^3.H^2O$, crystallises from aqueous solution by spontaneous evaporation, in fine octagonal plates, insoluble in ether, but soluble in boiling alcohol, whence it crystallises in white needles.

Dibromosulphanilic Acid, $C^6H^5Br^2NSO^3$ (Schmitt, *loc. cit.*).—Produced when 4 at. bromine are added to a hot solution of 1 at. sulphanilic acid:

$$C^6H^7NSO^3 + Br^4 = C^6H^5Br^2NSO^3 + 2HBr.$$

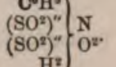
It remains in solution; is separated by filtration from the tribromaniline formed at the same time (p. 478); precipitated as a barium-salt by addition of barium-chloride;

and from this salt, purified by recrystallisation, the dibromosulphanilic acid is separated by sulphuric acid.

Dibromosulphanilic acid crystallises from aqueous solution in large colourless prisms, which contain $2C^6H^5Br^2NSO^3.3H^2O$, and give off their water of crystallisation gradually at ordinary temperatures, more quickly at 110°, becoming dull and opaque. It dissolves readily in *water*, whether hot or cold; sparingly in cold, more easily in hot *alcohol*. The concentrated aqueous solution, mixed with a small quantity of oil of vitriol, immediately yields the pure acid, in the form of a network of needles. The aqueous solution has a very sour and cooling taste: it gives a crystalline precipitate with *chloride of barium*, *acetate of lead*, and *nitrate of silver*. A concentrated solution warmed with *zinc*, gives off hydrogen, forming a zinc-salt, which separates out. The dehydrated acid bears a heat of 180° without alteration, but decomposes at a somewhat higher temperature, yielding tribromaniline and sulphurous anhydride, and leaving a difficultly combustible charcoal. It also gives off tribromaniline (not dibromaniline, as might be expected) when heated with potash or slaked lime. The aqueous solution is coloured brown by *chlorine*, and on heating the liquid, a pungent oil separates out.—*Nitrous acid* passed into the aqueous solution converts the acid into diazo-dibromosulphobenzolic acid, $C^6H^2Br^2N^2SO^3$.

The dibromosulphanilates crystallise in needles, and are more or less soluble in water.—The *barium-salt*, $C^{12}H^8Ba''Br^4N^2S^2O^6.2H^2O$, prepared as above, gives off its water at 110° without alteration of appearance, and does not decompose till very strongly heated.—The *lead-salt*, $C^{12}H^8Pb''Br^4N^2S^2O^6.2H^2O$, is permanent in the air, and gives off its water at 110°.—The *silver-salt*, $C^6H^4AgBr^2NSO^3$, forms somewhat reddish needles.—The *potassium-* and *sodium-salts*, obtained by decomposing the corresponding carbonates with the aqueous acid, are sparingly soluble in alcohol, and separate in needles on addition of alcohol to their aqueous solutions.—The *zinc-salt* is obtained, as above mentioned, by the action of the acid on metallic zinc.

Phenyldisulphamic or **Disulphanilic Acid,** $C^6H^7NS^2O^6$ =



$$\left.\begin{matrix}C^6H^3\\(SO^2)''\\(SO^2)''\\H^2\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}.$$

(Buckton and Hofmann, Chem. Soc. Qu. J. ix.—Carius, Zeitschr. Ch. Pharm. 1861, p. 632; Jahresb. 1861, p. 634.)—Two acids having this composition have been obtained, viz.—*a*. By heating sulphanilic acid (p. 477) with fuming sulphuric acid to 160° or 170°, for six or seven hours, till it assumes the consistence of treacle. On dissolving the syrupy residue in water, saturating with carbonate of barium, and evaporating the filtrate, a barium-salt is obtained, which after repeated solution in water, and evaporation under reduced pressure, remains as a mass of microscopic crystals, having, when dried at 190°—200°, the composition, $C^6H^5Ba''NS^2O^6$, showing that the acid is dibasic. From the lead-salt, prepared in a similar manner, the free acid, $C^6H^7NS^2O^6$, may be separated by the action of sulphydric acid. It has a very acid and pungent taste, is very difficult to crystallise, and is insoluble in alcohol, which precipitates it from strong solutions in white grains, especially on addition of a little ether.—The *silver-salt*, $C^6H^5Ag^2NS^2O^6$, prepared by neutralising the aqueous acid with carbonate of silver, crystallises from aqueous solution in small plates, and is precipitated by ether-alcohol in colourless crystalline grains. (Buckton and Hofmann.)

β. By the action of ammonium-sulphite on nitrobenzol (Carius):

$$\underset{\text{Nitrobenzol.}}{C^6H^5NO^2} + 3(NH^4)^2SO^3 = \underset{\beta\text{-Disulphanilate of Ammonium.}}{C^6H^5(NH^4)^2NS^2O^6} + \underset{\text{Sulphate of Ammonium.}}{(NH^4)^2SO^4} + H^2O + 2NH^3.$$

When 1 at. nitrobenzol and 3 at. neutral sulphite of ammonium are boiled together in dilute alcoholic solution, for six or eight hours, in such a manner that the condensed vapours may flow back again, and the resulting solution is evaporated, sulphate of ammonium separates out first, then laminar crystals of *β*-disulphanilate of ammonium, which are difficult to purify. It is best, therefore, to convert this salt, by treatment with baryta, into the *barium-salt*, $C^6H^5Ba''NS^2O^6$. This salt is easily soluble in water, insoluble in absolute alcohol, and crystallises in colourless prisms. It may be boiled, without decomposition, in neutral or alkaline solutions, as also may the other salts of the same acid; but on attempting to separate the *β*-disulphanilic acid from them, it splits up, by assumption of 1 at. water, into aniline and sulphuric acid:

$$C^6H^7NS^2O^6 + 2H^2O = C^6H^7N + 2H^2SO^4.$$

This decomposition, and the dissimilarity of the barium-salts of the two acids just described, shows that these acids are not identical, but only isomeric. The latter, from its mode of formation, and the mode of decomposition just mentioned, is probably the true phenyldisulphamic acid, $\left.\begin{matrix}C^6H^5\\(SO^2)''\\(SO^2)''\\H^2\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$; whereas the former, resulting from the action of sulphuric acid upon aniline (amidobenzol), may rather be regarded as amidodisulphobenzolic acid, $C^6H^5(NH^2)S^2O^6$.

Phenyldisulphodiamic Acid, $C^6H^8N^2S^2O^6 = \left.\begin{matrix}(C^6H^4)''\\(SO^2)^2\\H^2\end{matrix}\right\}\begin{matrix}N^2\\O^2\end{matrix}$.—*Dithiobenzolic Acid.* (Hilkenkamp, Ann. Ch. Pharm. xcv. 86; Jahresb. 1855, p. 636.)—Produced as an ammonium-salt, by the action of sulphite of ammonium on nitrobenzol, probably containing dinitrobenzol:

$$C^6H^4(NO^2)^2 + 6(NH^4)^2SO^3 = C^6H^6(NH^4)^2N^2S^2O^6 + 4(NH^4)^2SO^4 + 2NH^3.$$

The materials (80 grms. nitrobenzol, 340 grms. dry sulphite of ammonium, and 1 litre of anhydrous alcohol, together with a little carbonate of ammonium, to keep the mixture alkaline) were cohobated for several hours; and the liquid decanted from the sulphate of ammonium, which separated, was evaporated to an oily consistence; it then deposited a large quantity of white laminæ (doubtless consisting of phenyldisulphamate of ammonium), together with a small quantity of hard slender needles, consisting of the phenyldisulphodiamate, $C^6H^6(NH^4)^2N^2S^2O^6$. This salt is very soluble in water and in aqueous alcohol, sparingly soluble in absolute alcohol, insoluble in ether; when heated it chars, swells up, and emits the odour of sulphurous acid. Its aqueous solution is slightly acid.

All the phenyldisulphodiamates are easily soluble. The *barium-salt*, $C^6H^6Ba''N^2S^2O^6$, obtained by decomposing the ammonium-salt with baryta-water, forms crystalline crusts, insoluble in alcohol and ether.

Benzyldisulphamic Acid. $C^7H^9NS^2O^6 = \left.\begin{matrix}C^7H^7\\(SO^2)^2\\H^2\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$. *Tolyldisulphamic Acid. Thiotoluolsäure. Disulfuryl-toluylsäure.* (Hilkenkamp, *loc. cit.*—Carius, Zeitschr. Ch. Pharm. 1861, p. 632; Jahresb. 1861, p. 634.)—Obtained in the same manner as phenyldisulphamic acid, by the action of ammonium-sulphite on nitrobenzylene (nitrotoluol). According to Hilkenkamp, the *ammonium-salt*, which is the direct product of the reaction, has the composition $C^7H^8(NH^4)NS^2O^6$; and the *potassium-salt*, obtained by decomposing it with potash, contains $C^7H^8KNS^2O^6$; which would imply either that the acid is monobasic, or that these are acid salts. According to Carius, the *barium-salt*, obtained by decomposing the ammonium-salt with baryta-water, has the composition $C^7H^7Ba''NS^2O^6$, showing that the acid is dibasic, like phenyldisulphamic acid. The other benzyldisulphamates resemble the corresponding phenyl-compounds (p. 479), and the acid, when separated from them, splits up in like manner into sulphuric acid and benzylamine. (Carius.)

Cumenyldisulphamic Acid. $C^9H^{13}NS^2O^6 = \left.\begin{matrix}C^9H^{11}\\(SO^2)^2\\H^2\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$. *Disulfuryl-cumenylsäure.* (Carius, *loc. cit.*).—Prepared in like manner from nitrocumol. The salts are similar to the phenyldisulphamates, the barium-salt having the composition $C^9H^{11}Ba''NS^2O^6$, and the acid separated from it is resolved in like manner into sulphuric acid and cumenylamine.

SULPHAMIDE. $\left.\begin{matrix}(SO^2)''\\H^4\end{matrix}\right\}N^2$.—According to Regnault (Ann. Ch. Phys. [2] lxxix. 170), this body is produced, together with sal-ammoniac, when dry ammonia-gas is passed over sulphuric chloride, SO^2Cl^2; but, according to H. Rose, the product thus formed is a mixture of sal-ammoniac and neutral sulphamate of ammonium (sulphatammon).

SULPHAMIDIC ACID. See SULPHAZOTISED ACIDS (p. 482).

SULPHAMIDOBENZAMINE. $C^7H^8N^2S = \left.\begin{matrix}(C^7H^4S)''\\H^4\end{matrix}\right\}N^2$. (Hofmann, Proc. Roy. Soc. x. 598.)—This base, metameric with phenylsulphocarbamide, $[(CS)''(C^6H^5)H^3]N^2$ (i. 756), and analogous to Chancel's oxybenzodiamide (i. 755), is produced by the action of ammonium-sulphide on nitrobenzonitrile, $C^7H^4(NO^2)N$. When this compound is boiled with an aqueous solution of ammonium-sulphide, a large quantity of sulphur separates at first; and on evaporating the liquid, a yellowish oil is deposited, which solidifies but imperfectly, and is difficult to purify. This oil is a weak base, having the composition of amidobenzonitrile, $C^7H^6N^2 = C^7H^4(NH^2)N$; and by prolonged contact with ammonium-sulphide, it is gradually converted into sulphamidobenzamine:

$$\underset{\text{Nitrobenzo-nitrile.}}{C^7H^4(NO^2)N} + 3H^2S = 2H^2O + S^3 + \underset{\text{Amidobenzo-nitrile.}}{C^7H^6N^2}.$$

and

$$\underset{\text{Amidobenzo-nitrile.}}{C^7H^6N^2} + H^2S = \underset{\text{Sulphamido-benzamine.}}{C^7H^8N^2S}.$$

Sulphamidobenzamine is very soluble in alcohol and in ether, and crystallises from hot water in white shining needles. It dissolves easily in acids, and is precipitated therefrom by potash and ammonia. It forms a crystallisable hydrochlorate and an orange-yellow crystalline chloroplatinate.

SULPHAMIDOCHLOROBENZOIC ACID. $C^7H^4Cl(NH^2)SO^5$.—When chloramidobenzoic acid, $C^7H^4Cl(NH^2)O^2$ (obtained by the action of potassium-cyanide on ethylic chlorobenzoate), is treated with strong sulphuric acid, and the diluted solution is boiled with barium-carbonate, sulphamidochlorobenzoate of barium, $C^7H^2Ba''Cl(NH^2)SO^5$, is produced, and separates from the solution in nodular groups of crystals. (D. Cunze and H. Hübner, Ann. Ch. Pharm. cxxxv. 106; Jahresb. 1865, p. 330.)

SULPHAMIDONIC ACID. A syrupy deliquescent acid, produced by triturating starch with strong sulphuric acid. Its salts are all amorphous, deliquescent, easily soluble in water, and very unstable, so that their composition is difficult to determine. The *calcium-salt* appears to contain $C^{24}H^{46}Ca''O^{24}.2SO^3$. (Gm., xv. 104.—Gerhardt, ii. 549.)

SULPHAMMON. Syn. with SULPHATAMMON.

SULPHAMMONIC ACID. See SULPHAZOTISED ACIDS (p. 482).

SULPHAMYLIC ACID. See SULPHURIC ETHERS.

SULPHAN. A name proposed by Graham for the radicle SO^4.

SULPHANETHIC or **SULPHANETHOLIC ACID.** An acid produced by the action of strong sulphuric acid on anise-camphor (i. 297). Its soluble salts colour ferric solutions deep violet, almost black. The *barium-salt* appears to have the composition $Ba''O.2(C^{10}H^{12}O.SO^3)$. (Gerhardt, J. pr. Chem. xxxvi. 267.)

SULPHANILIC ACID. See SULPHAMIC ACID (p. 477).

SULPHANISIC ACID. See ANISIC ACID (i. 303).

SULPHANISOLIC ACID. $C^7H^8SO^4$. } Products formed by the action of sulphuric acid on anisol (i. 305).
SULPHANISOLIDE. $C^{14}H^{14}SO^4$.

SULPHANTIMONATES. } See ANTIMONY, SULPHIDES OF (i. 334, 335).
SULPHANTIMONITES.

SULPHARSENATES. } See ARSENIC, SULPHIDES OF (i. 388, 391).
SULPHARSENITES.

SULPHARSIN. Syn. with SULPHIDE OF CACODYL (i. 409).

SULPHASATHYDE or **SULPHASATYDE.** Syn. with SULPHISATYDE. (See ISATYDE, iii. 411.)

SULPHATAMMON. Neutral sulphamate of ammonium.

SULPHATES. See SULPHUR, OXYGEN-ACIDS OF.

SULPHATOXYGEN. Syn. with SULPHAN.

SULPHAZALIC, SULPHAZIDIC, SULPHAZILIC, SULPHAZINOUS, and **SULPHAZINIC ACIDS.** See SULPHAZOTISED ACIDS.

SULPHAZOBENZOYL, HYDRIDE OF. *Thiobenzaldin.* $C^{21}H^{19}NS^2$?—A product of the action of ammonia on hydride of thiobenzyl or sulphide of stilbene (i. 571):

$$3C^7H^6S + NH^3 = C^{21}H^{19}NS^2 + H^2S.$$

On mixing 1 vol. bitter-almond oil dissolved in 4 or 5 vols. ether with 1 vol. ammonium-sulphide, and leaving the ether to evaporate in a shallow vessel, the compound separates in large crystals, which melt at 123°, dissolve in 20 to 30 pts. of ether, and are decomposed by boiling alcohol, with evolution of sulphydric acid. (**Laurent**, Ann. Ch. Phys. [3] xxxvi. 342.)

SULPHAZOTISED ACIDS. (**Frémy**, Ann. Ch. Phys. [3] xv. 408; Handw. vii. 679.)—A series of acids, the potassium-salts of which are formed by the action of sulphurous anhydride upon a solution of potassium-nitrite containing a large excess of free alkali. Sulphurous anhydride combines with the elements of potassium-nitrite and water in several proportions, forming compounds which crystallise readily, and in which neither sulphurous nor nitrous acid can be detected by the usual tests. The solutions of these salts form, with salts of barium, precipitates containing the corresponding acids. These compounds are all decomposed by boiling their solutions, ammonia and sulphuric acid being found among the products; some of them even experience a similar decomposition at ordinary temperatures.

The derivation of some of these salts from potash, water, sulphurous and nitrous anhydrides, may be represented by the following formulæ:

Sulphazite of potassium, $3K^2O.S^3H^6N^2O^{12} = 3K^2O + N^2O^3 + 3SO^2 + 3H^2O$
Sulphazate „ $3K^2O.S^4H^6N^2O^{14} = 3K^2O + N^2O^3 + 4SO^2 + 3H^2O$
Sulphazotate „ $3K^2O.S^5H^6N^2O^{16} = 3K^2O + N^2O^3 + 5SO^2 + 3H^2O$
Sulphammonate „ $4K^2O.S^8H^6N^2O^{22} = 4K^2O + N^2O^3 + 8SO^2 + 3H^2O$

Sulphammonate of Potassium is formed by mixing the strong solutions of nitrite and sulphite of potassium; it is then deposited in beautiful silky needles.—The *sulphazate* is formed by the action of sulphurous anhydride on nitrite of potassium in alkaline solution; the *sulphazite* by the action of water on the sulphazate; the *sulphazotate* separates in large rhombohedral crystals, on evaporating an aqueous solution of the sulphazate. Neither of these acids can exist in the free state, *i. e.* as hydrogen-salts.

Frémy also describes:—*Metasulphazotate of potassium*, $3K^2O.S^8H^6N^2O^{22}$, formed, together with the sulphazotate, by the action of sulphurous anhydride on nitrite of potassium: acid not isolated.—*Sulphazilite*, $K^2O.S^2HNO$, produced by the action of silver-oxide in the cold on a solution of the neutral sulphazotate: acid not isolated.—*Metasulphazilite*, $3K^2O.S^6H^6N^2O^{20}$, formed in like manner at the boiling heat.—*Sulphamidate*, $K^2O.S^2H^3NO^5$, formed from the sulphammonate by the action of water: acid not isolated.—*Sulphazidic acid*, $2H^2O.S^2H^6N^2O^7$, is obtained by decomposing the barium-salt (the mode of preparation of which is not given) with an equivalent quantity of sulphuric acid. By saturating it with potash, the potassium-salt, $2K^2O.S^2H^6N^2O^7$, is obtained in regular six-sided laminæ.

SULPHESATYDE. Syn. with DISULPHISATYDE (iii. 412).

SULPHIDES and **SULPHYDRATES.** The term sulphide (formerly *sulphuret*), in its widest sense, includes all compounds in which sulphur forms the electronegative constituent. Sulphur unites in this way with all the metals, with most of the non-metallic elements, and with many organic radicles. The sulphides are, for the most part, analogous in composition to the oxides, and, like the latter, may be divided into acid and basic sulphides, or sulphur-acids and sulphur-bases, which are capable of uniting together and forming sulphur-salts. To the class of acid sulphides belong the sulphides of the non-metallic elements, and those metallic sulphides which are soluble in sulphide of ammonium—viz., the sulphides of antimony, arsenic, tin, molybdenum, tungsten, vanadium, gold, and platinum; the other metallic sulphides and the sulphides of the alcohol-radicles are basic.

METALLIC SULPHIDES.—Precisely as we have oxides and hydrates formed on the type of one or more atoms of water, so we have sulphides and sulphydrates derived from one or more atoms of sulphydric acid. The more or less basylous sulphides, like their corresponding oxides, may be divided into three principal classes, monatomic, diatomic, and triatomic, formed respectively on the types of one, two, and three atoms of sulphydric acid. The first class includes hemisulphides and protosulphides, with the corresponding sulphydrates. Hemisulphide of nickel, Ni^2S, sulphide of zinc, $Zn''S$, and sulphydrate of sodium, $HNaS$, may be taken as examples. The second class includes disulphides and disulphydrates. Disulphide of platinum, $Pt^{iv}S^2$, and sulphydrate of barium, $Ba''H^2S^2$, may be taken as examples. The third class includes the trisulphides with their corresponding sulphydrates, such as trisulphide of bismuth, Bi^2S^3, and trisulphide of chromium, Cr^2S^3. It is observable that while the trioxides constitute a most important class of oxides, the trisulphides are a very unimportant class of sulphides. As a rule, they do not occur native, are scarcely salifiable, and do not result from the ordinary analytical processes which produce the other metallic sulphides with such facility.

The sulphides differ much from one another in the rapidity and completeness with which they are decomposed by acids. When finely pulverised, they are all decomposed more or less perfectly by hydrochloric acid gas, but some of them are attacked very slowly by the boiling liquid acid. All salifiable sulphides, however, behave like their corresponding oxides, when decomposed by hydrochloric acid, and yield one atom of sulphydric acid for every atom of sulphur in the sulphide, thus:

$$\begin{aligned} Fe''S &+ 2HCl &= H^2S &+ Fe''Cl^2. \\ \overset{''}{Sn}{}^2S^2 &+ 4HCl &= 2H^2S &+ 2Sn''Cl^2. \\ \overset{'''}{Sb}{}^2S^3 &+ 6HCl &= 3H^2S &+ 2Sb'''Cl^3. \end{aligned}$$

With reference to the distinction between sulphides and sulphydrates, it may be observed that the sulphydrates of the basylous metals—lithium, sodium, potassium, calcium, strontium, barium, and magnesium—are well-defined compounds, which dissolve in water, forming colourless solutions. The solutions of the sulphydrates of magnesium and calcium are decomposed by ebullition, with evolution of sulphydric acid, thus: $Mg''H^2S^2 + 2H^2O = Mg''H^2O^2 + 2H^2S$. But the other sulphydrate solutions may be evaporated down, whereby they yield colourless transparent crystals of their respective sulphydrates. These basylous sulphydrates are usually made by saturating their corresponding hydrates with sulphydric acid gas. The dry alkaline sulphydrates, when heated to redness out of contact with air, are decomposed into sulphydric acid and metallic sulphide: $Ba''H^2S^2 = H^2S + Ba''S$; but the sulphydrates of potassium and sodium require a very strong heat to effect their decomposition. The sulphides of the acid-forming metals also appear to form definite sulphydrates, corresponding to their respective oxygen-acids; but the nature of these compounds, and still more of the sulphydrates of the intermediate metals, is not well established. It is not clear, for instance, whether the so-called hydrated sulphide of zinc consists of $Zn''H^2S^2$, or $Zn''S.H^2O$, or $Zn''H^2S^2.Zn''H^2O^2$. The hydrated sulphides of the ferric and plumbic families seem indeed not to be sulphydrates; for when soluble salts of the metals of these families are added to solutions of alkaline sulphydrates, sulphydric acid is evolved:

$$Fe''SO^4 + H^2O + 2KHS = K^2SO^4 + Fe''S.H^2O + H^2S.$$

Moreover, it is not clear that all sulphides precipitated from metallic solutions by excess of sulphydric acid, or a sulphydrate, are necessarily either hydrated or sulphydrated, despite their greater solubility in acids, and their difference in colour from the undoubtedly anhydrous sulphides made in the dry way. We know, for instance, that the difference between the native scarlet sulphide of mercury and the precipitated black sulphide, or that between the native grey sulphide of antimony and the precipitated orange sulphide, is not a difference of hydration at all, but one of molecular condition, *i. e.* allotropy.

The protosulphides of the alkali-metals and alkaline earth-metals dissolve in water, forming colourless solutions, from which, by evaporation, the solid sulphides may, it is said, be again procured, and in the crystalline state. It is not improbable that the solutions really contain mixtures of alkaline hydrate and sulphydrate, resulting from the reaction of the sulphide with water, thus: $K^2S + H^2O = KHS + KHO$. At any rate, precisely similar solutions are made by mixing equal quantities of alkaline hydrate and sulphydrate. With the exception of the above sulphides of the basylous metals, all sulphides and hydrated sulphides are insoluble in water, or very nearly so. Those which, like the trisulphide of arsenic, are sparingly soluble in pure water, are insoluble in acidulated water. This trisulphide, when recently precipitated, is slowly but completely decomposed, by boiling with water into arsenious and sulphydric acids.

As a rule, the sulphides and oxides of the same metal have similar formulæ, and correspond in their general behaviour. Occasionally, indeed, we have metallic oxides to which there are no corresponding sulphides (the peroxide of manganese, for example), and more frequently metallic sulphides to which there are no corresponding oxides, —the hemisulphide of iron and the disulphide of arsenic, for example. Among the sulphides to which there are no corresponding oxides, perhaps the most remarkable are the alkaline polysulphides. The metal potassium, for instance, is said to form the compounds K^2S, K^2S^2, K^2S^3, K^2S^4, and K^2S^5 (iv. 707).

When protosulphide of potassium is fused with excess of sulphur, the pentasulphide is formed as a dark liver-coloured mass which sinks beneath the excess of melted sulphur. It is a very definite compound, soluble in water, forming a deep orange liquid, which may also be obtained by boiling an excess of sulphur with a solution of the protosulphide. Its composition corresponds with that of the sulphate and hyposulphite or thiosulphate of potassium, thus:

K^2SO^4, Sulphate.
$K^2S^2O^3$, Thiosulphate.
K^2S^5, Pentasulphide.

It is doubtful whether the three intermediate polysulphides are other than mixtures of proto- and penta-sulphide. They may, however, be definite sulphides corresponding to the polythionic series of oxygen-salts, thus:

K^2S^2, Disulphide.	$K^2S^2O^6$, Dithionate.
K^2S^3, Trisulphide.	$K^2S^3O^6$, Trithionate.
K^2S^4, Tetrasulphide.	$K^2S^4O^6$. Tetrathionate.
K^2S^5, Pentasulphide.	$K^2S^5O^6$, Pentathionate.

It is observable, moreover, that the three intermediate polysulphides result from definite reactions, and that the disulphide and trisulphide correspond to definite oxides. The yellow colour, which solutions of alkaline protosulphide and sulphydrate acquire by exposure to air, is due to the production of polysulphides, thus: $2KHS + O = K^2S^2 + H^2O$. The yellow solutions of the polysulphides eventually become colourless by absorption of oxygen, which produces a thiosulphate, accompanied, in the case of the tri-, tetra-, and penta-sulphides, with a deposit of sulphur. The polysulphides do not appear to form corresponding polysulphydrates; for when sulphur is boiled with solutions of sulphydrates, there is always an evolution of sulphydric acid, thus:

$$2KHS + S = K^2S^2 + H^2S.$$

The distinction between neutral and salifiable sulphides is much less marked even than that between neutral and salifiable oxides. Disulphide of iron, for instance, is obviously the representative of the non-salifiable peroxide of manganese. The two compounds, when heated in close vessels, undergo precisely similar decompositions:

$$\begin{aligned} 3MnO^2 &= Mn^3O^4 + O^2. \\ 3FeS^2 &= Fe^3S^4 + S^2. \end{aligned}$$

On the other hand, the trisulphide of iron is obviously the representative of the salifiable trioxide of that metal, and should correspond with it in its reaction with hydrochloric acid, thus:

$$\begin{aligned} Fe^2O^3 + 6HCl &= 2FeCl^3 + 3H^2O. \\ Fe^2S^3 + 6HCl &= 2FeCl^3 + 3H^2S. \end{aligned}$$

But sulphydric acid has the property of reducing trichloride of iron to the state of dichloride, with a deposition of sulphur, thus: $2FeCl^3 + H^2S = 2FeCl^2 + 2HCl + S$. Hence the actual behaviour of trisulphide of iron, when treated with hydrochloric acid, corresponds, not with that of the salifiable trioxide of iron, but with that of the indifferent trioxide of cobalt:

$$\begin{aligned} Co^2O^3 + 4HCl &= 2CoCl^2 + 2H^2O + O. \\ Fe^2S^3 + 4HCl &= 2FeCl^2 + 2H^2S + S. \end{aligned}$$

The sulphides of the chlorous metals have characters corresponding to those of the corresponding metallic oxides; that is to say, they unite with the sulphides of the basylous metals to form corresponding soluble salts. The disulphide of tin, and the trisulphides and pentasulphides of antimony and arsenic, for instance, dissolve in sulphydrate of potassium or ammonium, just as the corresponding oxides dissolve in oxhydrate of potassium or ammonium. Thus we have stannate of potassium, K^2SnO^3 or $K^2O.SnO^2$, and sulphostannate of potassium, K^2SnS^3 or $K^2S.SnS^2$. When these chlorous sulphides dissolve in alkaline hydrates, they form both sulphosalts and oxysalts, thus:

$$3SnS^2 + 6KHO = 2K^2SnS^3 + K^2SnO^3 + 3H^2O.$$

Respecting the modes of formation and the reactions of metallic sulphides, see further METALS (iii. 940); also Odling's *Manual of Chemistry* (i. 153).

On the sulphides and sulphydrates of alcohol-radicles, see ETHERS (ii. 511).

The individual sulphides, inorganic and organic, are specially described in connection with the several elements and organic radicles.

SULPHINDIGOTIC ACID. See INDIGO-SULPHURIC ACIDS (iii. 258).

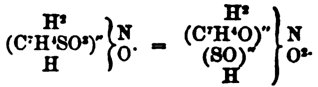
SULPHINDYLIC ACID. Syn. with SULPHINDIGOTIC ACID.

SULPHISATANOUS ACID. An acid produced, according to Laurent, by the action of ammonium-sulphite on disulphisatyde (iii. 412).

SULPHISATIN. Syn. with DISULPHISATYDE.

SULPHITES. See SULPHUR, OXYGEN-ACIDS OF.

SULPHOBENZAMIC ACID, $C^7H^7NSO^4$ =



$$C^7H^7NSO^4 = \left.\begin{matrix} H^2 \\ (C^7H^4SO^3)'' \\ H \end{matrix}\right\} \begin{matrix} N \\ O \end{matrix} = \left.\begin{matrix} H^2 \\ (C^7H^4O)'' \\ (SO)'' \\ H \end{matrix}\right\} \begin{matrix} N \\ O^2 \end{matrix}.$$

(Limpricht and Uslar, Ann. Ch. Pharm. cvi. 27; Jahresb. 1858, p. 275.—Engelhardt, Petersb. Acad. Bull. xvi. 378; Jahresb. 1858, p. 278.)—This acid, the amic acid of sulphobenzoic acid, is produced: 1. By heating sulphobenzamide, or ethylsulphobenzoate of ammonium, with potash (Limpricht and Uslar):

$$\underset{\text{Sulphobenzamide.}}{C^7H^8N^2SO^3} + H^2O = \underset{\text{Sulphobenzamic acid.}}{C^7H^7NSO^4} + NH^3.$$

Also from the compound $C^7H^6N^2SO^2$ (the hydrochlorate of which is formed by treating sulphobenzamide with pentachloride of phosphorus, p. 686), likewise with elimination of ammonia (Limpricht and Uslar):

$$C^7H^6N^2SO^2 + 2H^2O = C^7H^7NSO^4 + NH^3.$$

3. Together with other products, by the action of sulphuric anhydride on benzonitrile. (Engelhardt.)

Preparation.—1. Sulphobenzamide, stirred up to a paste with strong potash-ley, is heated in the water-bath for several hours, till a clear solution is obtained. This is diluted with water, and supersaturated with hydrochloric acid, whereby the sulphobenzamic acid is obtained as a bulky precipitate, which is purified by recrystallisation from boiling water. (Limpricht and Uslar.)

2. Vapour of sulphuric anhydride is slowly passed into well-cooled benzonitrile, whereby a crystalline mass is produced (if the action goes on more quickly, a vitreous mass is formed, which yields other products). On treating the crystalline mass with cold water, to remove excess of sulphuric acid, and dissolving the residue in boiling alcohol, needle-shaped crystals separate at first, but afterwards, on addition of ether, rhombohedral crystals of sulphobenzamic acid. (Engelhardt.)

Properties.—Sulphobenzamic acid crystallises from a boiling saturated solution on cooling, in scales resembling chlorate of potassium (Limpricht and Uslar); in rhombohedral crystals or in needles, consisting of aggregates of small rhombohedrons (Engelhardt). It is very sparingly soluble in cold water, more soluble in ether, easily in hot water and in alcohol. It melts at a temperature above 200°, and solidifies in a crystalline mass on cooling; at a higher temperature it volatilises in white vapours, and finally burns with a luminous flame. It reddens litmus, decomposes carbonates, but does not dissolve zinc.

Decompositions.—1. Sulphobenzamic acid appears to be resolved by prolonged heating into ammonia and sulphobenzoic anhydride. The aqueous solution, when evaporated, leaves sulphobenzoic acid.—2. When 1 at. sulphobenzamic acid is heated to 150°—200° with 1½ at. *pentachloride of phosphorus*, as long as phosphoric oxychloride continues to distil over, a yellow oily liquid is left, consisting of sulphobenzamic chloride, $C^7H^6NSO^3Cl$, which is converted by water into hydrochloric and sulphobenzamic acids, ($C^7H^6NSO^3Cl + H^2O = HCl + C^7H^7NSO^4$), and by ammonia into sulphobenzamide (Limpricht and Uslar). By distilling sulphobenzamic acid with *pentachloride of phosphorus*, a distillate is obtained, containing—besides oxychloride of phosphorus—chlorobenzonitrile, chlorobenzoic chloride (in small quantity), and the chloride of an easily soluble acid, probably isomeric with sulphobenzamic acid.

The same chloride appears to be obtained, together with amorphous sulphobenzamic acid, by heating 1 at. sulphobenzamic acid with 1 at. of the pentachloride. On treating the yellow tumefied residue with ether, the amorphous sulphobenzamic acid remains as a white pulverulent mass, which is insoluble in water, alcohol, and ether, but is converted, by heating with water to 170°—180°, into ordinary crystallised sulphobenzamic acid. (Limpricht and Uslar.)

3. Sulphobenzamic acid treated with *sulphuric anhydride* yields a brown viscid mass, from which, by boiling with plumbic carbonate, a salt is obtained, having the composition of plumbic sulphobenzoate.

Sulphobenzamates.—Sulphobenzamic acid is monobasic. All its salts are more or less soluble in water.—The *ammonium-salt* separates in laminar crystals, on evaporating a solution of the acid in ammonia.—The *barium-salt*, $C^{14}H^{12}Ba''N^2S^2O^8.4H^2O$, separates from the evaporated neutral solution as a soft, wavellitic, crystalline mass, which gives off its water at 110°.—The *calcium-salt*, dried at 120°, has the composition $C^{14}H^{12}Ca''N^2S^2O^8$.—The *silver-salt*, $C^7H^6AgNSO^4.H^2O$, is precipitated by silver-nitrate from the solution of the ammonium-salt, in slender silky needles; it may be recrystallised from boiling water, and does not blacken on exposure to light.

The solution of the ammonium-salt gives, with *neutral lead-acetate*, a precipitate, crystallising in small needles; with *ferrous salts* a white, with *ferric salts* a flesh-coloured, precipitate; with *cupric salts*, a precipitate consisting of small needles, soluble in ammonia; with *mercurous salts*, a white precipitate turning black on boiling; with *mercuric chloride*, a crystalline precipitate separating from water in laminæ; with *zinc-salts* no precipitate.

Ethylic Sulphobenzamate, or *Sulphobenzamic Ether*, $C^7H^6(C^2H^5)NSO^4$, is obtained by passing hydrochloric acid gas into the alcoholic solution of the acid; by decomposing the silver-salt with ethylic iodide; or by treating the alcoholic solution of sulphobenzoic chloride with ammonia-gas. It crystallises in splendid shining needles, which, according to Keferstein, are monoclinic prisms, ∞P . ∞P∞ . oP . —P, having their axes in the ratio of 1 : 2 : 4. When cautiously heated, it melts without decomposition, and solidifies in the crystalline state on cooling; at a higher temperature it gives off white fumes, and burns with a bright flame. It dissolves easily in warm alcohol or ether, somewhat less easily in boiling water. Strong caustic potash dissolves it, at ordinary temperatures, without evolution of ammonia; at 100° with formation of alcohol and potassic sulphobenzamate; at higher temperatures also with evolution of ammonia. It does not dissolve mercuric oxide, and only a small quantity of silver-oxide. (Limpricht and Uslar.)

SULPHOBENZAMIDE. $C^7H^8N^2SO^3 = \left.\begin{matrix}(C^7H^4SO^2)''\\H^4\end{matrix}\right\}N^2 = \left.\begin{matrix}(C^7H^4O)''\\(SO)''\\H^4\end{matrix}\right\}\begin{matrix}N^2\\O\end{matrix}$ (Limpricht and Uslar, Ann. Ch. Pharm. cii. 239; cvi. 27.—Jahresb. 1857, p. 336; 1858, p. 275.)—Obtained by treating sulphobenzoic chloride with strong aqueous ammonia. The product, washed with water, dried, and recrystallised from absolute alcohol, with addition of animal charcoal, yields anhydrous sulphobenzamide; if aqueous alcohol be used, a mixture of the anhydrous amide and a hydrate containing 1 at. water is obtained.

Sulphobenzamide dissolves readily in hot water and hot alcohol. The hydrate, which crystallises in needles, gives off its water at 100°; at 170° the compound fuses, and between 270° and 290° it slowly decomposes, but without formation of sulphobenzimide.—When treated with *potash*, it gives off ammonia, and is converted into sulphobenzamic acid (p. 485).—With *pentachloride of phosphorus* at 100°, it decomposes, according to the equation:

$$C^7H^8N^2SO^3 + PCl^5 = C^7H^6N^2SO^2.HCl + POCl^3 + HCl;$$

forming a yellow syrup, which is further decomposed during the distillation, yielding phosphoric oxychloride and chlorobenzonitrile. The compound $C^7H^6N^2SO^2.HCl$ dissolves in ether and in alcohol, but does not crystallise therefrom; with water or ammonia, however, it yields the crystallisable compound $C^7H^6N^2SO^2$, which dissolves in potash, and by prolonged heating therewith is converted into sulphobenzamic acid.

SULPHOBENZANILIDE. *Diphenylsulphobenzamide*, $C^7H^6(C^6H^5)^2SO^3$, is produced by mixing sulphobenzoic chloride with aniline. When crystallised from alcohol, with aid of animal charcoal, it forms small white fusible crystals, easily soluble in alcohol and ether, slightly soluble in cold water, decomposed by hot potash-ley with separation of aniline.

SULPHOBENZIDE. $C^{12}H^{10}SO^2$. (Mitscherlich, Pogg. Ann. xxxi. 628.—Freund, Ann. Ch. Pharm. cxx. 76.—Otto, *ibid.* cxxxv. 154.)—A compound formed, together with phenylsulphurous acid, by the action of sulphuric anhydride on benzol. On treating the thick liquid product with a large quantity of water, the sulphobenzide separates in the crystalline form, while the phenylsulphurous acid remains in solution. The sulphobenzide may be purified by crystallisation from ether, or by distillation (Mitscherlich). It is also produced, together with benzol, by distilling aqueous phenylsulphurous acid, and crystallises in the receiver. (Freund.)

Sulphobenzide crystallises from alcohol in rhombic plates. It melts at 100° (Mitscherlich), at 128° (Freund), at 128°—129° (Otto), and boils at a much higher temperature. It dissolves in *alcohol* and in *ether*, is insoluble in *alkalis*, but dissolves in *acids*, and is precipitated therefrom by water. Strong *sulphuric acid* dissolves it when heated, and converts it into phenylsulphurous acid. *Chlorine* converts it, at the boiling heat, into trichlorobenzol (Mitscherlich).—With *pentachloride of phosphorus* it forms monochlorobenzol, chloride of sulphophenyl, and trichloride of phosphorus (Otto):

$$C^{12}H^{10}SO^2 + PCl^5 = C^6H^5Cl + C^6H^5SO^2Cl + PCl^3.$$

SULPHOBENZIDIC ACID. Syn. with PHENYLSULPHUROUS ACID.

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2. By the action of sulphuric acid on benzonitrile, disulphobenzolic acid being formed at the same time:

$$\underset{\text{Benzo-}}{C^7H^5N} + H^2O + 2H^2SO^4 = \underset{\substack{\text{Sulpho-}\\ \text{benzoic}\\ \text{acid.}}}{C^7H^6SO^5} + (NH^4.H)SO^4.$$

$$\underset{\substack{\text{Benzo-}\\ \text{nitrile.}}}{C^7H^5N} + 3H^2SO^4 = \underset{\substack{\text{Disulpho-}\\ \text{benzolic}\\ \text{acid.}}}{C^6H^6S^2O^6} + (NH^4.H)SO^4 + CO^2.$$

On neutralising the product of the reaction with carbonate of barium, evaporating, redissolving in water, and adding alcohol by separate portions, sulphobenzoate of barium crystallises out first, and afterwards the disulphobenzolate. (**Buckton** and **Hofmann**, Chem. Soc. Qu. J. ix. 255.)

3. By the action of water on sulphobenzoic chloride:

$$C^7H^4SO^3Cl^2 + 2H^2O = C^7H^6SO^5 + 2HCl.$$

Sulphobenzoic acid forms a solid crystalline mass, which may be heated to 150° without decomposition: it deliquesces gradually in damp air, but recovers its solid form in a dry atmosphere. It is not altered by boiling with acids or alkalis, but on fusing it with *solid potash*, the sulphur is converted, partly into sulphuric, partly into sulphurous acid.—By a mixture of 2 pts. oil of vitriol and 1 pt. nitric acid, it is converted into nitrosulphobenzoic acid, $C^7H^5(NO^2)SO^5$.—With 2 at. pentachloride of phosphorus, it forms sulphobenzoic chloride:

$$C^7H^6SO^5 + 2PCl^5 = C^7H^4SO^3Cl^2 + 2POCl^3 + 2HCl.$$

With 1 at. of the pentachloride, the product is sulphobenzoic chlorhydrate:

$$C^7H^6SO^5 + PCl^5 = C^7H^4SO^3\left\{\begin{matrix}Cl\\ HO\end{matrix}\right. + POCl^3 + HCl.$$

Sulphobenzoates.—Sulphobenzoic acid is dibasic, forming acid and neutral salts, the former being for the most part less soluble than the latter.—The *neutral barium-salt*, $C^7H^4Ba''S^2O^5$, obtained by boiling the solution of the acid salt with barium-carbonate, forms indistinct crystals, very soluble in water, and bearing without decomposition a temperature as high as that of boiling oil.—The *acid barium-salt*, $C^7H^4Ba''SO^5.C^7H^6SO^5.3H^2O$, prepared as above described, crystallises in monoclinic prisms: oP . ∞P . ∞P∞, with the angles oP : ∞P = 98°6′; ∞P : ∞P = 82° 21 (**Fehling**). The crystals give off their water at 200°, dissolve in 20 pts. water at 20°, and have an acid reaction.—The *lead-salt*, $C^7H^4Pb''SO^5.2H^2O$, is obtained in solution by boiling the acid with excess of lead-carbonate, and separates on cooling in stellate groups of slender needles. Gives off its water at 200°.—The *neutral potassium-salt*, $C^7H^4K^2SO^5$, forms beautiful deliquescent crystals: the *acid salt* is efflorescent.—The *silver-salt*, $C^7H^4Ag^2SO^5.H^2O$, crystallises in a vacuum in small yellowish prisms, which dissolve easily in water, and give off 1 at. water when dried. (**Fehling.**)

The acid sulphobenzoates of magnesium and zinc, also the acid ferrous, cobaltous, and cupric salts, form beautiful crystals. (**Mitscherlich.**)

Derivatives of Sulphobenzoic Acid.

Nitrosulphobenzoic Acid, $C^7H^5(NO^2)SO^5$. (**Limpricht** and **Uslar.**)—Prepared by adding sulphobenzoic or sulphobenzamic acid to a cold mixture of strong nitric and sulphuric acids, diluting with water after some time, neutralising with carbonate of barium, and decomposing the resulting barium-salt with sulphuric acid. It crystallises from a concentrated solution in well-defined crystals.—The *neutral barium-salt*, $C^7H^3Ba''(NO^2)SO^5$, forms easily soluble, nodular, mostly yellowish crystals, containing 3 or $\frac{3}{2}$ at. water.—The *acid barium-salt*, $C^7H^3Ba''(NO^2)SO^5$.

Ethylic Sulphobenzamate, or *Sulphobenzamic Ether*, $C^7H^6(C^2H^5)NSO^4$, is obtained by passing hydrochloric acid gas into the alcoholic solution of the acid; by decomposing the silver-salt with ethylic iodide; or by treating the alcoholic solution of sulphobenzoic chloride with ammonia-gas. It crystallises in splendid shining needles, which, according to Keferstein, are monoclinic prisms, ∞P . ∞P∞ . oP . —P, having their axes in the ratio of 1 : 2 : 4. When cautiously heated, it melts without decomposition, and solidifies in the crystalline state on cooling; at a higher temperature it gives off white fumes, and burns with a bright flame. It dissolves easily in warm alcohol or ether, somewhat less easily in boiling water. Strong caustic potash dissolves it, at ordinary temperatures, without evolution of ammonia; at 100° with formation of alcohol and potassic sulphobenzamate; at higher temperatures also with evolution of ammonia. It does not dissolve mercuric oxide, and only a small quantity of silver-oxide. (Limpricht and Uslar.)

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On neutralising the product of the reaction with carbonate of barium, evaporating, redissolving in water, and adding alcohol by separate portions, sulphobenzoate of barium crystallises out first, and afterwards the disulphobenzolate. (**Buckton** and **Hofmann**, Chem. Soc. Qu. J. ix. 255.)

3. By the action of water on sulphobenzoic chloride:

$$C^7H^4SO^3Cl^2 + 2H^2O = C^7H^6SO^5 + 2HCl.$$

Sulphobenzoic acid forms a solid crystalline mass, which may be heated to 150° without decomposition: it deliquesces gradually in damp air, but recovers its solid form in a dry atmosphere. It is not altered by boiling with acids or alkalis, but on fusing it with *solid potash*, the sulphur is converted, partly into sulphuric, partly into sulphurous acid.—By a mixture of 2 pts. oil of vitriol and 1 pt. nitric acid, it is converted into nitrosulphobenzoic acid, $C^7H^5(NO^2)SO^5$.—With 2 at. pentachloride of phosphorus, it forms sulphobenzoic chloride:

$$C^7H^6SO^5 + 2PCl^5 = C^7H^4SO^3Cl^2 + 2POCl^3 + 2HCl.$$

With 1 at. of the pentachloride, the product is sulphobenzoic chlorhydrate:

$$C^7H^6SO^5 + PCl^5 = C^7H^4SO^3\left\{\begin{matrix}Cl\\HO\end{matrix}\right. + POCl^3 + HCl.$$

Sulphobenzoates.—Sulphobenzoic acid is dibasic, forming acid and neutral salts, the former being for the most part less soluble than the latter.—The *neutral barium-salt*, $C^7H^4Ba''S^2O^6$, obtained by boiling the solution of the acid salt with barium-carbonate, forms indistinct crystals, very soluble in water, and bearing without decomposition a temperature as high as that of boiling oil.—The *acid barium-salt*, $C^7H^4Ba''SO^5.C^7H^6SO^5.3H^2O$, prepared as above described, crystallises in monoclinic prisms: oP . ∞P . ∞P∞, with the angles oP : ∞P = 98°6′; ∞P : ∞P = 82° 21 (**Fehling**). The crystals give off their water at 200°, dissolve in 20 pts. water at 20°, and have an acid reaction.—The *lead-salt*, $C^7H^4Pb''SO^5.2H^2O$, is obtained in solution by boiling the acid with excess of lead-carbonate, and separates on cooling in stellate groups of slender needles. Gives off its water at 200°.—The *neutral potassium-salt*, $C^7H^4K^2SO^5$, forms beautiful deliquescent crystals: the *acid salt* is efflorescent.—The *silver-salt*, $C^7H^4Ag^2SO^5.H^2O$, crystallises in a vacuum in small yellowish prisms, which dissolve easily in water, and give off 1 at. water when dried. (**Fehling**.)

The acid sulphobenzoates of magnesium and zinc, also the acid ferrous, cobaltous, and cupric salts, form beautiful crystals. (**Mitscherlich**.)

Derivatives of Sulphobenzoic Acid.

Nitrosulphobenzoic Acid, $C^7H^5(NO^2)SO^5$. (**Limpricht** and **Uslar**.)—Prepared by adding sulphobenzoic or sulphobenzamic acid to a cold mixture of strong nitric and sulphuric acids, diluting with water after some time, neutralising with carbonate of barium, and decomposing the resulting barium-salt with sulphuric acid. It crystallises from a concentrated solution in well-defined crystals.—The *neutral barium-salt*, $C^7H^3Ba''(NO^2)SO^5$, forms easily soluble, nodular, mostly yellowish crystals, containing 3 or $\frac{3}{2}$ at. water.—The *acid barium-salt*, $C^7H^3Ba''(NO^2)SO^5$.

$C^7H^5(NO^2)SO^5$, crystallises in small, limpid, radiating prisms, containing 4 at. water. —The *silver-salt*, obtained by boiling the acid with silver-oxide, crystallises in small nodules, easily soluble in water, insoluble in alcohol.

Amidosulphobenzoic Acid, $C^7H^7NSO^5 = C^7H^5(NH^2)SO^5$, produced by continued digestion of nitrosulphobenzoic acid with aqueous sulphide of ammonium, separates, on supersaturating the concentrated filtrate with hydrochloric acid, in white concentrically-grouped needles, having an acid reaction, easily soluble in hot water, less soluble in alcohol, nearly insoluble in ether. When heated, it chars without previous fusion. It dissolves easily in ammonia, and the solution forms, with nitrate of silver, a white precipitate, which turns black on boiling. Amidosulphobenzoic acid does not appear to unite with other acids, at least not with hydrochloric acid. (Limpricht and Uslar.)

SULPHOBENZOIC CHLORHYDRATE. $C^7H^5ClSO^4 = C^7H^4SO^3\left\{\begin{matrix}Cl\\HO\end{matrix}\right. = \left.\begin{matrix}(C^7H^4O)''\\(SO)''\\H\end{matrix}\right\}\begin{matrix}Cl\\O^2\end{matrix}$. *Chlorwasserstoff-Sulfobenzoesäure.*—This compound, analogous to Williamson's sulphuric chlorhydrate, $SO^2.Cl.HO$, is obtained:—1. By heating 1 at. sulphobenzoic acid with 1 at. pentachloride of phosphorus, till the greater part of the phosphoric oxychloride has distilled off, and adding water to the residue to dissolve out hydrochloric and phosphoric acids.—2. By leaving sulphobenzoic chloride in contact with water for several weeks:

$$C^7H^4Cl^2SO^3 + H^2O = C^7H^5ClSO^4 + HCl.$$

It is a white crystalline powder, soluble in ether, decomposed by alcohol and by boiling water, insoluble in cold water. It melts very easily, and decomposes at a higher temperature. By boiling water and by alkalis it is converted into sulphobenzoic acid. (Limpricht and Uslar.)

SULPHOBENZOIC CHLORIDE. $C^7H^4SO^3Cl^2 = \left.\begin{matrix}(C^7H^4O)''\\(SO)''\end{matrix}\right\}\begin{matrix}Cl^2\\O\end{matrix}$.—Prepared like the preceding, but with 2 at. phosphoric pentachloride to 1 at. sulphobenzoic acid dried at 100°. It is a yellowish-brown, viscid, oily liquid, having a faint unpleasant odour, heavier than water, and very slowly decomposed thereby. Boiling water dissolves it more quickly, forming hydrochloric and sulphobenzoic acids.—*Alkalis* decompose it in a similar manner. When heated to 300° it decomposes with strong intumescence, giving off chloride of chlorobenzoyl (i. 567), and leaving a carbonaceous mass.—*Alcohol* dissolves it, with great rise of temperature and formation of ethylic sulphobenzoate. Anhydrous ether appears to dissolve it without decomposition.—Aqueous *ammonia* converts it into sal-ammoniac and sulphobenzamide: the latter is also formed by passing ammonia-gas into the ethereal solution of the chloride.—With *aniline* it forms sulphobenzanilide and hydrochlorate of aniline. *Alcohol* saturated with *ammonia*, dissolves it with great rise of temperature, forming ethylsulphobenzoic acid. (Limpricht and Uslar.)

SULPHOBENZOIC ETHERS. The only ones known are the acid and neutral ethylic ethers.

Ethylic Sulphobenzoate, $C^{11}H^{14}SO^5 = C^7H^4(C^2H^5)^2SO^5$. (Limpricht and Uslar, Ann. Ch. Pharm. cii. 252.)—Absolute alcohol becomes strongly heated in contact with sulphobenzoic chloride; hydrochloric acid and chloride of ethyl are given off; and on evaporating the liquid over the water-bath, ethylic sulphobenzoate remains in the form of a syrupy residue having a faint ethereal odour. It dissolves in water in all proportions, and cannot therefore be purified, like most compound ethers, by washing with water. On heating the aqueous solution, the ether is resolved into alcohol and sulphobenzoic acid. It cannot be distilled without decomposition; when heated in a retort, it leaves a large quantity of charcoal; swells up considerably, and yields a small quantity of distillate having a disagreeable odour. Treated with gaseous or aqueous ammonia, it yields ethylsulphobenzoate of ammonium.

Ethylsulphobenzoic Acid, $C^9H^{10}SO^5 = C^7H^5(C^2H^5)SO^5$. (Limpricht and Uslar, *loc. cit.*)—Produced in the form of an ammonium-salt, by dissolving sulphobenzoic chloride in alcoholic ammonia, or by dissolving sulphobenzoic ether in alcohol, and passing ammonia through the solution. On evaporating the liquid, the ammonium-salt is obtained in crystals; and by dissolving these in water, precipitating the ammonia with platinic chloride, removing the excess of platinum by sulphuretted hydrogen, and evaporating the filtrate at the heat of the water-bath, ethylsulphobenzoic acid is obtained, in the form of a yellowish syrup, which does not show any signs of crystallisation, even after standing for several days. The acid appears, however, to be crystallisable, but difficult to obtain in the crystalline form, on account of its proneness to decomposition; for on decomposing the barium-salt with an equivalent quantity of sulphuric acid, and evaporating the filtrate over the water-bath, a syrup was obtained, which solidified in a crystalline mass on cooling, but on being saturated with barium-carbonate, yielded a mixture of sulphobenzoate and ethylsulphobenzoate of barium.

The *Ethylsulphobenzoates* are all very soluble: they are most readily prepared from the ammonium-salt by precipitating the ammonia with platinic chloride, removing the excess of platinum with sulphydric acid, and neutralising the filtrate with the required base.—The *ammonium-salt*, $C^9H^9(NH^4)SO^5$, crystallises in large, well-defined, four-sided tables, with very distinct cleavage parallel to the shorter side of the base. It is insoluble in ether, but dissolves readily in water and in alcohol, forming neutral solutions.—The *barium-salt*, $C^{18}H^{18}Ba''S^2O^{10}.xH^2O$, crystallises from a very concentrated aqueous solution, in small rhombic tables, which effloresce over oil of vitriol.—The *silver-salt* forms stellate groups of small needles.—The *sodium-salt*, $C^9H^9NaSO^5$, forms nodular groups of milk-white needles, easily soluble in water and in alcohol.

SULPHOBENZOL. C^7H^6S. Syn. with SULPHIDE OF BENZYLENE (i. 577).

SULPHOBENZOLAMIDE. $C^6H^7NSO^2 = N.H^2.C^6H^5SO^2$. (Stenhouse, Proc. Roy. Soc. xiv. 351.)—Produced by heating sulphobenzolate (phenylsulphite) of ammonium to 200°. Crystallises from alcohol or water in laminæ resembling naphthalene, which melt at 153°.

SULPHOBENZOLENE. $C^6H^{10}SO^2$. (Stenhouse, *loc. cit.*)—A compound isomeric with sulphobenzide (p. 486), produced by heating phenylic sulphide (iv. 417) with strong nitric acid, or more readily by digesting it with acid potassium-chromate and sulphuric acid diluted with 2 pts. of water. When crystallised from benzol, it forms monoclinic prisms, exhibiting the combination $[\infty P\infty] . \infty P\infty . Pn . oP$, with the angles (approximately determined) $[\infty P\infty] : \infty P\infty = 85° 30'$ and $94° 30'$; $[\infty P\infty] : Pn = 71° 40'$; $\infty P\infty : oP = 69° 40'$. The crystals are tabular, from predominance of $[\infty P\infty]$. From hot alcohol it separates in crystals, resembling chlorate of potassium, but for the most part of the same form and with the same angles as from benzol. It dissolves easily in ether and in carbonic disulphide, but with difficulty in boiling water, from which it crystallises completely on cooling. It melts at 126°, and distils at a higher temperature. It dissolves in hot sulphuric acid, and is precipitated therefrom by water. A mixture of nitric and sulphuric acids converts it into an oxidation-product, sparingly soluble in hot alcohol, and crystallising in needles.

SULPHOBENZOLENIC ACID. Syn. with BENZYLSULPHUROUS ACID. (See SULPHUROUS ETHERS.)

SULPHOBENZOLIC ACID. Syn. with PHENYLSULPHUROUS ACID. (See SULPHUROUS ETHERS.)

Disulphobenzolic Acid. Syn. with PHENYLENE-SULPHUROUS ACID. (See SULPHUROUS ETHERS.)

SULPHOBENZOLIC CHLORIDE. Syn. with SULPHOPHENYLIC CHLORIDE.

SULPHOBENZOYL, HYDRIDE OF. C^7H^6S. A compound formed by the action of ammonium-sulphide on an alcoholic solution of bitter-almond oil (i. 571).

SULPHOBUTYLIC ACID. Syn. with TETRYLSULPHURIC ACID. (See SULPHURIC ETHERS.)

SULPHOCACODYLIC ACID. See ARSENIDES OF METHYL (i. 409).

SULPHOCAMPHIC ACID. Syn. with THYMYLSULPHUROUS ACID. (See SULPHUROUS ETHERS.)

SULPHOCAMPHORIC ACID. $C^9H^{16}SO^6$. (Walter, Ann. Ch. Phys. [3], ix. 177.)—An acid produced by the action of sulphuric acid on camphoric anhydride (i. 730):

$$C^{10}H^{14}O^3 + H^2SO^4 = C^9H^{16}SO^6 + CO.$$

To prepare it, camphoric anhydride is introduced by small portions into an excess of strong sulphuric acid, and the clear solution is heated to 65°. Carbonic oxide is then rapidly evolved, and the liquid, after being left at rest to deposit unaltered camphoric anhydride, then filtered and left to evaporate in a vacuum, deposits crystals of sulphocamphoric acid, sometimes having a green colour. For purification they are left to drain in a funnel plugged with asbestos, then pressed between bibulous paper, and crystallised several times from alcohol till they become colourless.

Sulphocamphoric acid crystallises in six-sided prisms, colourless, very bitter, very soluble in water, alcohol, and ether. The crystals contain 2 at. water, which they give off in a vacuum. The acid melts between 160° and 165°, and decomposes at a higher temperature. It dissolves slowly in cold, quickly in boiling nitric acid, without alteration or evolution of red fumes. Strong sulphuric acid dissolves and ultimately chars it.

Sulphocamphoric acid is dibasic, its neutral salts being represented by the formula $C^9H^{14}M^2SO^6$.—The *ammonium-salt*, $C^9H^{14}(NH^4)^2SO^6.H^2O$, forms stellate groups of crystals, which are very soluble in water, and redden litmus.—The *potassium-salt*, $C^9H^{14}K^2SO^6$, crystallises by evaporation in very fine needles, having a cooling styptic taste. It is neutral to test-papers, very soluble in water, slightly soluble in alcohol. Sometimes cauliflower-heads of crystals are obtained, apparently consisting of an acid salt.—The *barium-salt*, $C^9H^{14}Ba''SO^6$, forms a colourless or slightly yellow gummy mass, which faintly reddens litmus-paper, is very soluble in water, slightly soluble in alcohol.—A *bario-cupric salt*, $C^{18}H^{28}Ba''Cu''S^2O^{12}$, is obtained by precipitating a cold solution of the barium-salt with cupric sulphate.—The *lead-salt*, $C^9H^{14}Pb''SO^6$, is an amorphous mass, having a sweet taste, soluble in water, insoluble in alcohol, reddening litmus-paper.—The *silver-salt*, $C^9H^{14}Ag^2SO^6$, is obtained, by saturating the acid with silver-oxide and evaporating, in crystalline crusts, soluble in water, slightly soluble in cold, somewhat more in hot alcohol: this salt likewise reddens litmus.

SULPHOCAPRYLIC ACID. Syn. with OCTYLSULPHURIC ACID. (See SULPHURIC ETHERS.)

SULPHOCARBAMIC ACID. $CH^3NS^2 = \left.\begin{matrix}H^2\\(CS)''\\H\end{matrix}\right\}\begin{matrix}N\\S.\end{matrix}$ (Zeise, Ann. Ch. Pharm. xlviii. 95.—Debus, *ibid.* lxxiii. 26.)—The sulphur-analogue of carbamic acid (i. 749). Its ammonium-salt, $CH^2(NH^4)NS^2$, is produced:—1. By direct combination of ammonia with carbonic disulphide: $CS^2 + 2NH^3 = CH^6N^2S^2$. When a mixture of 1 vol. absolute alcohol saturated with ammonia-gas and a solution of 0·16 vol. carbonic disulphide in 0·4 vol. alcohol, is exposed in a closed flask to a temperature of 15°, it gradually turns brown, and deposits plumose crystals of ammonium-trisulphocarbonate, afterwards larger and more shining prismatic crystals of the sulphocarbamate. The liquid, after it has ceased to deposit crystals, yields a further quantity of the sulphocarbamate by distillation.

2. By the decomposition of ammonium-trisulphocarbonate:

$$\left.\begin{matrix}(CS)''\\(NH^4)^2\end{matrix}\right\}S^2 = \left.\begin{matrix}H^2\\(CS)''\\NH^4\end{matrix}\right\}\begin{matrix}N\\S\end{matrix} + H^2S.$$

To effect this transformation, the trisulphocarbonate is enclosed for 30 or 40 hours with alcohol in a well-closed flask.

Sulphocarbamic acid is obtained in the free state by decomposing the ammonium-salt with dilute sulphuric or hydrochloric acid. It then separates as a colourless or reddish oil, heavier than water, and having a peculiar odour, somewhat like that of sulphydric acid. It is somewhat unstable, being gradually resolved into sulphocyanic and sulphydric acids; in presence of water, it also yields cyanic acid or its products of decomposition:

$$\underset{\text{Sulphocarbamic acid.}}{CH^3NS^2} = \underset{\text{Sulphocyanic acid.}}{CHNS} + H^2S.$$

$$CH^3NS^2 + H^2O = \underset{\text{Cyanic acid.}}{CHNO} + 2H^2S.$$

Metallic Sulphocarbamates.—Sulphocarbamic acid is monobasic; it decomposes carbonates with effervescence. Its salts are easily resolved, especially by heat or by the action of alkalis, into sulphydric acid, sulphocyanic acid, and motallic sulphide:

$$\underset{\text{Sulphocarbamate.}}{2H^2(CS)''MSN} = \underset{\text{Sulphocyanic acid.}}{2(CS)'HN} + H^2S + M^2S.$$

Sulphocarbamate of Ammonium, $CH^2(NH^4N)S^2$, crystallises in long lemon-yellow prisms, easily soluble in water, less soluble in alcohol. Exposed to moist air it deliquesces, and is converted into a liquid, consisting almost entirely of ammonium-sulphydrate. Heated with *potash*, it yields sulphocyanate and sulphide of potassium, together with water and ammonia. *Chlorine*, *bromine*, and *iodine* convert it into hydranzotin or sulphocarbammonium-sulphide (iii. 178):

$$2CH^2(NH^4)NS^2 + Cl^2 = 2NH^4Cl + C^2H^4N^2S^4.$$

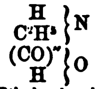
Ammonium-sulphocarbamate. Hydranzotin.

The same transformation is effected by ferric salts mixed with excess of sulphuric or hydrochloric acid.

Cuprous Sulphocarbamate, $CH^2Cu'NS^2$, is a yellow powder, insoluble in water and in alcohol.—The *lead-salt*, $C^2H^4Pb''N^2S^4$, is precipitated by neutral lead-acetate from the solution of the ammonium-salt, in white flocks, which turn red on drying and blacken when boiled with water.—The *zinc-salt*, $C^2H^4Zn''N^2S^4$, is a white pulverulent precipitate.

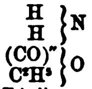
A solution of ammonium-sulphocarbamate is not precipitated by calcium- or barium-salts. It forms a yellowish-green precipitate with *nickel-sulphate*, white with *mercuric chloride*, yellowish-brown with *platinic chloride*; with a dilute solution of *silver-nitrate* a yellow precipitate, which soon turns black. A mixture of the concentrated solutions of ammonium-sulphocarbamate and *chromic sulphate* deposits, after a while, a small quantity of colourless needles containing chromium and sulphur; and the mother-liquor, after some hours, deposits a blue substance.

SULPHOCARBAMIC ETHERS. Sulphocarbamic acid, like other amic acids, may give rise to two isomeric groups of ethers, according as an atom of hydrogen belonging to the ammonia-type or to the water-type in the formula, $\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}N\\\left.\begin{matrix}(CS)''\\H\end{matrix}\right\}S\end{matrix}$, is replaced by an alcohol-radicle, the relation between the two groups being the same as that which exists between ethylcarbamic acid and ethylic carbamate (i. 750, 751):



$$\begin{matrix}\left.\begin{matrix}H\\C^2H^5\end{matrix}\right\}N\\\left.\begin{matrix}(CO)''\\H\end{matrix}\right\}O\end{matrix}$$

Ethylcarbamic acid.



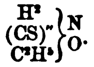
$$\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}N\\\left.\begin{matrix}(CO)''\\C^2H^5\end{matrix}\right\}O\end{matrix}$$

Ethylic carbamate.

To the first-mentioned group of sulphocarbamic ethers belong amylsulphocarbamic acid, $\left.\begin{matrix}C^5H^{11}.H\\(CS)''\\H\end{matrix}\right\}\begin{matrix}N\\S\end{matrix}$, and its amylammonium-salt, $\left.\begin{matrix}C^5H^{11}.H\\(CS)''\\NH^3(C^5H^{11})\end{matrix}\right\}\begin{matrix}N\\S\end{matrix}$, the latter being produced by the action of amylamine on carbonic disulphide, and the amylcarbamic acid separated from it by hydrochloric acid (see AMYLAMINES, i. 207); also allyl-sulphocarbamic or sulphosinapic acid (*q.v.*).

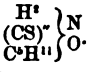
Ethers derived from sulphocarbamic acid, CH^3NS^2, by the substitution of an alcohol-radicle for the hydrogen of the water-type have not yet been obtained; but two compounds are known, which may be derived in this manner from the unknown oxysulphocarbamic acid, CH^3NSO, viz.:

Ethylic Oxysulphocarbamate or Xanthamide . . . C^3H^7NSO =



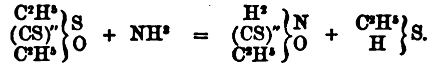
$$\left.\begin{matrix}H^2\\(CS)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O.\end{matrix}$$

Amylic Oxysulphocarbamate or Xanthamylamide . . $C^6H^{13}NSO$ =



$$\left.\begin{matrix}H^2\\(CS)''\\C^5H^{11}\end{matrix}\right\}\begin{matrix}N\\O.\end{matrix}$$

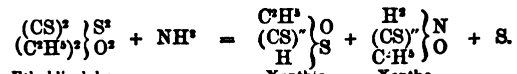
Ethylic Oxysulphocarbamate or **Xanthamide,** C^3H^7NSO. (Debus, Ann. Ch. Pharm. lxxii. 1; lxxv. 127; lxxxii. 253.)—This compound is produced:—1. By the action of ammonia on neutral ethylic disulphocarbonate (xanthic ether):



$$\left.\begin{matrix}C^2H^5\\(CS)''\\C^2H^5\end{matrix}\right\}\begin{matrix}S\\O\end{matrix} + NH^3 = \left.\begin{matrix}H^2\\(CS)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix} + \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}S.$$

Xanthic ether. Xanthamide. Mercaptan.

2. By the action of ammonia on ethyldisulphocarbonic sulphide (p. 495):



$$\left.\begin{matrix}(CS)^2\\(C^2H^5)^2\end{matrix}\right\}\begin{matrix}S^2\\O^2\end{matrix} + NH^3 = \left.\begin{matrix}C^2H^5\\(CS)''\\H\end{matrix}\right\}\begin{matrix}O\\S\end{matrix} + \left.\begin{matrix}H^2\\(CS)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix} + S.$$

Ethyldisulphocarbonic sulphide. Xanthic acid. Xanthamide.

To prepare the compound in considerable quantity, Debus gradually adds carbonic disulphide to an alcoholic solution of potash till the liquid is completely neutral, then dilutes it with two volumes of water, and passes chlorine into it. The chlorine decomposes the xanthate of potassium, forming chloride of potassium and ethyldisulphocarbonic sulphide, which, being insoluble in the dilute alcohol, falls to the bottom. As this compound is easily decomposed by an excess of chlorine, it is advisable to add to the liquid a small quantity of potassium-iodide, which will not be decomposed as long as there is any xanthate present, but will impart a brown colour to the liquid as soon as the whole of the xanthate is decomposed. The oily ethyldisulphocarbonic sulphide is then washed with water, dissolved in a mixture of 1 pt. ether and 2 pts. alcohol; and dry ammonia-gas is passed into the solution, whereby it gradually becomes turbid, and deposits long needles of sulphur. The filtered liquid, evaporated in a vacuum, leaves a saline residue, consisting of ammonium-xanthate and xanthamide, the latter of which may be dissolved out by ether, and remains, on evaporation, as a yellow oil, which ultimately crystallises, and may be obtained pure by recrystallisation from a small quantity of alcohol.

Xanthamide crystallises by spontaneous evaporation in monoclinic prisms or octahedrons, often of considerable size. Dominant faces, +P and −P with oP. Angle oP : −P = 118°; oP : +P = 105°. The plane angles of oP are nearly = 90°. Cleavage perfect, parallel to oP. The crystals melt at about 36°, dissolve sparingly in water, but are dissolved in all proportions by alcohol and ether.

Xanthamide is resolved by distillation into mercaptan and cyanic acid (or at 150°, cyanuric acid):

$$\underset{\text{Xanthamide.}}{CSO.C^2H^5.H^2N} = \underset{\text{Mercaptan.}}{C^2H^6S} + \underset{\text{Cyanic acid.}}{COHN.}$$

When boiled with *potash* or *baryta-water*, it is resolved into alcohol and sulphocyanic acid:

$$CSO.C^2H^5.H^2N = C^2H^6O + CSHN.$$

When *nitrous acid vapour* is passed into water containing xanthamide in suspension, a crystallisable substance is formed, designated by Debus as oxysulphocyanate of ethyl; its composition is approximately represented by the formula $C^6H^{10}N^4O^2S$, and it is probably formed by the union of 2 at. xanthamide, with elimination of hydrogen and sulphydric acid:

$$2C^3H^7NOS - H^2S - H^2 = C^6H^{10}N^2O^2S.$$

Compounds of Xanthamide with Metallic Salts.—α. With *cuprous chloride*, xanthamide forms four compounds, containing 1, 2, 3, and 4 at. xanthamide to 1 at. CuCl.

The compound $C^3H^7NOS.CuCl$, is obtained as a white crystalline precipitate, on adding hydrochloric acid to an aqueous solution of xanthamide mixed with excess of cupric sulphate. It is nearly insoluble in water, but dissolves in hot alcohol, and crystallises on cooling in small very brilliant rhombohedrons, approaching very closely to the cube. It is likewise formed on mixing an alcoholic solution of xanthamide with a neutral solution of cupric chloride. The liquid first becomes blood-red, then colourless, strongly acid, and deposits sulphur; and the filtrate yields, by spontaneous evaporation, first rhombohedral crystals of the compound $C^3H^7NOS.CuCl$, then long needles of the compound above mentioned as oxysulphocyanate of ethyl.

The compound $2C^3H^7NOS.CuCl$ is deposited, in shining rhombic tables, on adding rather more than 1 at. xanthamide to the preceding compound, and evaporating. It is insoluble in water, very soluble in alcohol, and appears to be dimorphous, inasmuch as a concentrated alcoholic solution deposits it in large hexagonal prisms, whereas from a dilute solution it separates in rhombic tables.

By increasing the proportion of xanthamide, the compounds $3C^3H^7NOS.CuCl$ and $4C^3H^7NOS.CuCl$ may be obtained, both in well-defined crystals. All these compounds are more fusible and more soluble in alcohol, as they contain a larger proportion of xanthamide. The crystals decompose after some weeks, sulphide of copper being set free.

β. With *Cuprous Iodide.*—A boiling alcoholic solution of the compound, $3C^3H^7NOS.CuCl$, mixed with a hot solution of iodide of potassium, deposits, after some hours, concentrically-grouped needles of the compound $2C^3H^7NOS.CuI$; the mother-liquor, on further concentration, yields laminæ of the compound $3C^3H^7NOS.CuI$; and the liquid finally deposits xanthamide and chloride of potassium.

γ. With *Cuprous Sulphocyanate.*—An alcoholic solution of the compound $2C^3H^7NOS.CuCl$, mixed with sulphocyanate of potassium, yields a white crystalline precipitate, which appears to consist of $C^3H^7NOS.10CyCuS$ (?). A hot concentrated solution of the compound $3C^3H^7NOS.CuCl$ yields, with sulphocyanate of potassium, an immediate precipitate, consisting of colourless tables of the compound $2C^3H^7NOS.3CyCuS$. If this compound be left immersed in the mother-liquor for some days, the crystals become larger, acquire a yellowish colour, and are converted into the compound $C^3H^7NOS.CyCuS$.

An alcoholic solution of the compound $C^3H^7NOS.CuCl$ yields with sulphocyanate of potassium, nothing but a white pulverulent precipitate of cuprous sulphocyanate.

δ. With *other Salts*.—The compound $3C^3H^7NOS.CuCl$ is decomposed at the boiling heat by zinc, which precipitates the copper and forms chloride of zinc; but this salt does not combine with the xanthamide, neither does xanthamide appear to unite with ferrous chloride, chloride of barium, or chloride of potassium. With *mercuric chloride*, however, it appears to be capable of forming, under certain circumstances, compounds similar to those which it yields with cuprous chloride.

Amylic Oxysulphocarbamate, Amylxanthamide, or **Xanthamylamide,** $C^6H^{13}NOS = CSO.C^5H^{11}.H^2N$.—This compound, discovered by M. W. Johnson (Chem. Soc. Qu. J. v. 242), and prepared similarly to the ethyl-compound, has been already described among the sulphur-compounds of amyl (i. 206).

SULPHOCARBAMIDE. $CH^4N^2S = \left.\begin{matrix}(CS)''\\H^2\\H^2\end{matrix}\right\}N^2$.—This compound has not yet been obtained. It contains the elements of sulphocyanate of ammonium, $CNS.NH^4$, but is not actually formed from that compound in the same manner as carbamide (urea) from cyanate of ammonium.

Several substitution-derivatives of sulphocarbamide are however known, and have been already described under CARBAMIDE (i. 754), viz.:

Allylsulphocarbamide	$N^2.(CS)''.C^3H^5.H^3$
Naphthyl-allylsulphocarbamide	$N^2.(CS)''.C^{10}H^7.C^3H^5.H^2$
Phenylsulphocarbamide	$N^2(CS)''.C^6H^5.H^3$
Diphenylsulphocarbamide	$N^2.(CS)''.(C^6H^5)^2.H^2$
Phenyl-allylsulphocarbamide	$N^2.(CS)''.C^6H^5.C^3H^5.H^2$.

These compounds are formed by the action of ammonia and alcoholic ammonia on sulphocyanic ethers; and compounds of analogous constitution, but having half the nitrogen replaced by phosphorus, are obtained by the action of triethylphosphine on the sulphocyanates of allyl and phenyl (iv. 611), *e.g.*:

$$\underset{\text{Triethyl-phosphine.}}{P(C^2H^5)^3} + \underset{\text{Phenylic sulphocyanate.}}{(CS)''(C^6H^5)N} = \underset{\text{Phenyl-triethyl-sulphocarbo-phosphamide.}}{\left.\begin{matrix}N\\P\end{matrix}\right\}(CS)''.C^6H^5.(C^2H^5)^3}.$$

SULPHOCARBIMIDE. $\left.\begin{matrix}(CS)''\\H\end{matrix}\right\}N$.—This is the compound more generally called sulphocyanic acid, and otherwise formulated as $\left.\begin{matrix}CN\\H\end{matrix}\right\}S''$. That this acid may really be regarded as the imide of sulphocarbonic acid is shown:—1. By its formation from sulphocarbamic acid, $(CS^2H^3N = CSHN + H^2S)$, and in the decomposition of sulphocarbamic ethers (p. 492).—2. By its formation when carbonic disulphide is heated in a sealed tube with alcoholic ammonia:

$$(CS)''S + NH^3 = \left.\begin{matrix}(CS)''\\H\end{matrix}\right\}N + H^2S;$$

and by the analogous formation of ethylic sulphocyanate, when ethylamine is substituted for ammonia in this reaction.

SULPHOCARBONATES. Carbonic disulphide, CS^2, unites directly with metallic sulphides, forming compounds called trisulphocarbonates, or simply sulphocarbonates, analogous to the carbonates, and represented by the general formula $M^2S.CS^2$ or M^2CS^3.

They are likewise produced, together with carbonates, by the action of carbonic disulphide on hydrated metallic oxides, *e.g.* with aqueous potash:

$$3CS^2 + 6KHO = 2K^2CS^3 + K^2CO^3 + 3H^2O$$

The sulphocarbonates of the alkali-metals and alkaline earth-metals are red, brown, or yellow compounds, soluble in water and in alcohol, and in some cases crystallisable. They are easily converted into carbonates, by boiling their aqueous solutions, water being decomposed and sulphydric acid evolved, *e.g.*:

$$K^2CS^3 + 3H^2O = 3H^2S + K^2CO^3.$$

A similar decomposition takes place slowly in the aqueous solution at ordinary temperatures.

By decomposing a metallic sulphocarbonate with hydrochloric acid, hydric sulphocarbonate, or sulphocarbonic acid, H^2CS^3, is obtained in the form of a yellow oily liquid, thus:

$$K^2CS^3 + 2HCl = 2KCl + H^2CS^3.$$

The sulphocarbonates of the heavy metals are insoluble in water, and are formed by precipitation. Solutions of the alkaline sulphocarbonates give a brown precipitate with cupric salts, yellow with dilute solutions of argentic nitrate and mercuric chloride, red with lead-salts. A solution of calcic sulphocarbonate forms, with auric chloride, a greyish-brown precipitate containing $Au^2S^3.3CS^2$; with platinic salts, a black-brown precipitate containing $PtS^2.2CS^2$. All these precipitates blacken more or less quickly when kept, owing to their conversion into sulphides.

For details respecting the metallic sulphocarbonates, see *Gmelin's Handbook* (vols. iii., iv., v., and vi.), under the several metals.

SULPHOCARBONIC ACID. This term belongs properly to the compound H^2CS^3, obtained as above; but it is sometimes applied to carbonic disulphide, CS^2, which should rather be called carbonic sulphanhydride.

SULPHOCARBONIC ETHERS. These are bodies having the composition of carbonic ethers (i. 799), in which the oxygen is replaced, wholly or partly, by sulphur. The following table exhibits their names and formulæ, the ethyl- and ethylene-compounds being taken as examples:

Ethyl-monosulphocarbonic acid	$CO^2S\left\{\begin{matrix}C^2H^5\\H\end{matrix}\right.$	=	$\left.\begin{matrix}C^2H^5\\(CO)''\\H\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$
Ethylic monosulphocarbonate	$CO^2S\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.$	=	$\left.\begin{matrix}C^2H^5\\(CO)''\\C^2H^5\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$
Ethyl-disulphocarbonic acid	$COS^2\left\{\begin{matrix}C^2H^5\\H\end{matrix}\right.$	=	$\left.\begin{matrix}C^2H^5\\(CS)''\\H\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$
Ethylic disulphocarbonate	$COS^2\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.$	=	$\left.\begin{matrix}C^2H^5\\(CS)''\\C^2H^5\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$
Ethyl-trisulphocarbonic acid	$CS^3\left\{\begin{matrix}C^2H^5\\H\end{matrix}\right.$	=	$\left.\begin{matrix}C^2H^5\\(CS)''\\H\end{matrix}\right\}\begin{matrix}S\\S\end{matrix}$
Ethylic trisulphocarbonate	$CS^3\left\{\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right.$	=	$\left.\begin{matrix}C^2H^5\\(CS)''\\C^2H^5\end{matrix}\right\}\begin{matrix}S\\S\end{matrix}$
Ethylenic disulphocarbonate	$COS^2.C^2H^4$	=	$\left.\begin{matrix}(CS)''\\(C^2H^4)''\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$
Ethylenic trisulphocarbonate	$CS^3.C^2H^4$	=	$\left.\begin{matrix}(CS)''\\(C^2H^4)''\end{matrix}\right\}S^2.$

It is not at present known with certainty whether the mono- and disulphocarbonic ethers contain the radicle CO or CS—whether, for example, ethyldisulphocarbonic acid should be regarded as $\left.\begin{matrix}C^2H^5\\(CS)''\\H\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$, or as $\left.\begin{matrix}C^2H^5\\(CO)''\\H\end{matrix}\right\}S^2$; but the formulæ above given are those which accord best with the principal reactions of these compounds.

Formation and Reactions.—*a.* The metallic salts of the acid sulphocarbonic ethers are produced in the same manner as those of the oxycarbonic ethers (i. 801): thus carbonic dioxide unites with sulphethylate (mercaptide) of potassium, to form ethyl-monosulphocarbonate of potassium, just as it unites with ethylate of potassium to form the ethyl-carbonate; and, in like manner, carbonic disulphide acts on ethylate of potassium or alcoholic potash, so as to form ethyl-disulphocarbonate of potassium; and on mercaptide of potassium, or an alcoholic solution of the sulphydrate, so as to form the ethyl-trisulphocarbonate, thus:

$CO^2 + (C^2H^5)KO = (C^2H^5)KCO^3.$ Ethyl-carbonate.
$CO^2 + (C^2H^5)KS = (C^2H^5)KCO^2S.$ Ethyl-monosulphocarbonate.
$CS^2 + (C^2H^5)KO = (C^2H^5)KCOS^2.$ Ethyl-disulphocarbonate.
$CS^2 + (C^2H^5)KS = (C^2H^5)KCS^3.$ Ethyl-trisulphocarbonate.

β. The neutral sulphocarbonic ethers (containing monatomic alcohol-radicles), are produced by the action of the chlorides, bromides, &c. of alcohol-radicles on the metallic salts of the corresponding acid ethers, *e.g.*:

$$\underset{\substack{\text{Potassic ethyl-}\\\text{trisulphocarbo-}\\\text{nate.}}}{(C^2H^5)KCS^3} + C^2H^5Cl = KCl + \underset{\substack{\text{Ethylic trisul-}\\\text{phocarbonate.}}}{(C^2H^5)^2CS^3.}$$

γ. The same **neutral ethers** are decomposed by hydrate or sulphydrate of potassium, especially in alcoholic solution, yielding a salt of an acid sulphocarbonic ether, together with alcohol or mercaptan; *e.g.:*

$$\begin{aligned}(C^2H^5)^2CO^2S + KHO &= (C^2H^5)HO + (C^2H^5)KCO^2S.\\(C^2H^5)^2CO^2S + KHS &= (C^2H^5)HS + (C^2H^5)KCO^2S.\\(C^2H^5)^2COS^2 + KHS &= (C^2H^5)HS + (C^2H^5)KCOS^2.\\(C^2H^5)^2COS^2 + KHO &= (C^2H^5)HS + (C^2H^5)KCO^2S.\end{aligned}$$

δ. Ethyldisulphocarbonic acid is resolved by heating (to 24°) into alcohol and carbonic disulphide:

$$(C^2H^5)HCOS^2 = (C^2H^5)HO + CS^2.$$

The decomposition of the free acid is therefore represented by an equation exactly similar to that by which its potassium-salt is formed: it is likewise analogous to that of ethylcarbonic acid (i. 801); but in the latter case the decomposition takes place spontaneously at ordinary temperatures, whereas ethyldisulphocarbonic acid may be separated in the free state from its salts, and decomposes only when heated.

ε. When iodine acts on a metallic salt of an acid sulphocarbonic ether (an ethylsulphocarbonate, for example) in alcoholic solution, peculiar compounds are formed, called **ethylsulphocarbonic sulphides**. A molecule of iodine acts on two molecules of the ethylsulphocarbonate, abstracting the two atoms of metal, while the residues of the two molecules of ethylsulphocarbonate remain united, forming ethylsulphocarbonic sulphide; *e.g.:*

$$\underset{\substack{\text{Potassic ethyl-}\\\text{disulphocarbonate.}}}{2(C^2H^5)KCOS^2} + I^2 = 2KI + \underset{\substack{\text{Ethyl-disulpho-}\\\text{carbonic sul-}\\\text{phide.}}}{(C^2H^5O)^2C^2S^4.}$$

$$\underset{\substack{\text{Potassic ethyl-mono-}\\\text{sulphocarbonate.}}}{2(C^2H^5)KCO^2S} + I^2 = 2KI + \underset{\substack{\text{Ethyl-monosul-}\\\text{phocarbonic}\\\text{sulphide.}}}{(C^2H^5S)^2C^2O^4.}$$

These bodies may be regarded as compounds of carbonic dioxide or disulphide with alcoholic peroxides and persulphides, just as the ordinary sulphocarbonic ethers may be regarded as compounds of carbonic dioxide or disulphide with alcoholic protoxides and protosulphides.

They are decomposed by heat, yielding a neutral sulphocarbonic ether, together with carbonic oxide, dioxide, or disulphide and free sulphur; *e.g.:*

$$\underset{\substack{\text{Ethyl-disul-}\\\text{phocarbonic}\\\text{sulphide.}}}{C^6H^{10}O^2S^4} = \underset{\substack{\text{Ethylic mono-}\\\text{sulphocarbo-}\\\text{nate.}}}{(C^2H^5)^2CO^2S} + CS^2 + S.$$

or:

$$\underset{\substack{\text{Ethyl-disulpho-}\\\text{carbonic sulphide.}}}{C^6H^{10}O^2S^4} = \underset{\substack{\text{Ethylic disul-}\\\text{phocarbonate.}}}{(C^2H^5)^2COS^2} + CO + S^2.$$

$$\underset{\substack{\text{Ethyl-mono-}\\\text{sulphocarbo-}\\\text{nic sulphide.}}}{C^6H^{10}O^4S^2} = \underset{\substack{\text{Ethylic mono-}\\\text{sulphocarbo-}\\\text{nate.}}}{(C^2H^5)^2CO^2S} + CO^2 + S.$$

They are also decomposed by hydrate or sulphydrate of potassium, sulphur being separated, and the potassium-salt of the corresponding acid sulphocarbonic ether being produced.

ζ. The **sulphocarbonic ethers of diatomic alcohol-radicles** are formed by the action of diatomic alcoholic bromides, iodides, &c., on sulphocarbonate of sodium; *e.g.:*

$$\left.\begin{matrix}(CS)''\\Na^2\end{matrix}\right\}S^2 + (C^2H^4)''Br^2 = 2NaBr + \left.\begin{matrix}(CS)''\\(C^2H^4)''\end{matrix}\right\}S^2.$$

These ethers are oxidised by fuming nitric acid, yielding diatomic sulphurous ethers; *e.g.:*

$$\underset{\substack{\text{Ethylenic}\\\text{disulpho-}\\\text{carbonate.}}}{\left.\begin{matrix}CS\\C^2H^4\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}} + O^6 = \underset{\substack{\text{Ethylenic}\\\text{sulphite.}}}{\left.\begin{matrix}SO\\C^2H^4\end{matrix}\right\}O^2} + CO^2 + SO^2.$$

Sulphocarbonic Ethers containing Monatomic Alcohol-radicles.

α. Allyl-compounds.

Allyl-disulphocarbonic Acid, $C^4H^6OS^2 = \left.\begin{matrix}C^3H^5\\(CS)''\\H\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$.—The potassium-salt of this acid is obtained, in yellow needles, by treating allylic alcohol with potash and carbonic disulphide. (Hofmann and Cahours, i. 146.)

Allylic Trisulphocarbonate, $C^7H^{10}S^3 = \left.\begin{matrix}(CS)''\\(C^3H^5)^2\end{matrix}\right\}S^3$. (Hüsemann, Ann. Ch. Pharm. cxxvi. 269.)—Produced by the action of allylic iodide on sodium-trisulphocarbonate at ordinary temperatures, in the same manner as the corresponding ethyl-compound. It is a yellow oily liquid, having an extremely pungent and offensive odour; specific gravity = 0·943; boiling-point between 170° and 175°. It is converted by strong nitric acid into allylsulphurous acid, and by ammonia into sulphocyanate of ammonium and sulphydrate of allyl.

β. Amyl-compounds.

Amyl-disulphocarbonic or **Xanthamylic Acid,** $C^6H^{12}OS^2 = \left.\begin{matrix}C^5H^{11}\\(CS)''\\H\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$. (De Koninck, Bull. de l'Acad. de Bruxelles [2], ix. 546.—Erdmann, J. pr. Chem. xxxi. 1.—Balard, Ann. Ch. Phys. [3], xii. 307.—M. W. Johnson, Chem. Soc. Qu. J. v. 142.)—The potassium-salt of this acid is obtained by the action of carbonic disulphide on a solution of potash in amylic alcohol; and on treating this salt with hydrochloric acid, the xanthamylic acid separates as a colourless or pale-yellow oily liquid, having a very disagreeable pungent odour; it must be dried over chloride of calcium, to preserve it from decomposition. It reddens litmus strongly, burns with a very bright flame, colours the skin deep yellow, and appears to be somewhat heavier than water.

Amyldisulphocarbonate, or *Xanthamylate of Ammonium* (obtained in the preparation of xanthamylamide, p. 493), crystallises from alcohol and ether in colourless prisms, which may be sublimed by careful heating. It is decomposed by water, slowly also by exposure to the air, yielding, among other products, sulphocyanate of ammonium and a yellow oil.—The *potassium-salt,* $C^6H^{11}KOS^2$, prepared as above, solidifies to a magma of crystalline scales, having a pale-yellow colour and nacreous lustre. It dissolves in water, alcohol, and ether, and precipitates many metallic solutions.

The *cuprous salt* is obtained by precipitation with cupric sulphate, in lemon-yellow flocks.—The *lead-salt,* $C^{12}H^{22}Pb''O^2S^4$, is a yellowish-white precipitate, which blackens when boiled. On adding an alcoholic solution of lead-acetate to a strong solution of the ammonium-salt mixed with a large quantity of alcohol, and leaving the liquid to evaporate, xanthamylate of lead separates in small shining laminæ (Johnson).—The *mercurous salt,* obtained by precipitation with mercuric chloride, is white, and does not blacken on boiling.—The *silver-salt* is a white precipitate, which blackens on boiling and on exposure to light.

Amyl-disulphocarbonic Sulphide, $C^{12}H^{22}O^2S^4 = (C^5H^{11}O)^2C\,S^4 = (C^5H^{11}S)^2C^2O^2S^2$. *Amyldioxysulphocarbonate.* (M. W. Johnson, Chem. Soc. Qu. J. v. 142.)—Produced by the action of iodine on xanthamylates (p. 495). Hydrate of potassium is triturated in a mortar with amylic alcohol and carbonic disulphide, avoiding an excess of amylic alcohol; and the product, after being mixed with a little water, is treated with powdered iodine. The reaction takes place rapidly, and amyl-disulphocarbonic sulphide separates as a yellowish odorous oil, which must be washed, and then dried over chloride of calcium. It begins to boil at 187°, and decomposes, yielding, amongst other products, an oil having the composition of amylic disulphocarbonate. With ammonia it yields amyldisulphocarbonate (xanthamylate) of ammonium, amylic sulphocarbamate (xanthamylamide), and a deposit of sulphur:

$$C^{12}H^{22}O^2S^4 + NH^3 = \underset{\text{Xanthamy-lic acid.}}{C^6H^{12}OS^2} + \underset{\text{Xanthamyl-amide.}}{C^6H^{13}NOS} + S.$$

Amylic Disulphocarbonate, $C^{11}H^{22}OS^2 = \left.\begin{matrix}(CS)''\\(C^5H^{11})^2\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$. *Xanthamylic Ether.* (Desains, Ann. Ch. Phys. [2], xx. 505.)—Obtained by distilling the product of the action of iodine on xanthamylate of potassium. It is an amber-coloured oil, having a strong ethereal odour.

Methylamylic Disulphocarbonate, $(CH^3)(C^5H^{11})COS^2$, is obtained, according to Johnson, by distilling a mixture of amyldisulphocarbonate and methylsulphate of potassium. When digested with ammonia, it yields xanthamylamide.

Ethylamylic Disulphocarbonate, $(C^2H^5)(C^5H^{11})COS^2$, obtained in like manner, is a yellow oil.

Amylic Trisulphocarbonate, $C^{11}H^{22}S = \left.\begin{matrix}(CS)''\\(C^5H^{11})^2\end{matrix}\right\}S^2$. (Hüsemann, Ann. Ch. Pharm. cxxvi. 269).—Prepared, like the corresponding ethyl-compound (p. 500), by the action of amylic iodide in alcoholic solution on trisulphocarbonate of sodium. It is a yellowish oily liquid, having an unpleasant odour, insoluble in water, soluble in alcohol, ether, chloroform, and benzol. Specific gravity = 0·877. Boiling-point between 245° and 248°.

γ. *Cetyl-compound.*

Cetyldisulphocarbonic Acid, $C^{17}H^{34}OS^2 = (C^{16}H^{33})HCOS^2$. *Sulphocarbocetic Acid. Xanthocetic Acid.* (Desains and De la Provostaye, Ann. Ch. Phys. [3], vi. 494.)—Known only as a potassium-salt, $C^{17}H^{33}KOS^2$, which is prepared by adding pulverised potassium-hydrate to cetylic alcohol saturated with carbonic disulphide, and gently heating the pasty mass, which forms after some hours, with four times its volume of alcohol of 40°, keeping the temperature below the boiling-point. The solution on cooling deposits the salt in bulky flakes, which may be purified by successive washing with alcohol and ether. After drying in the air, it forms a very fine crystalline powder, having a faint odour, and unctuous to the touch; it is very hygroscopic, but is not wetted by water. When digested with hydrochloric acid it reproduces cetylic alcohol.

The alcoholic solution of the potassium-salt forms, with *mercuric chloride*, a white precipitate; with *acetate of lead* a white, and with *nitrate of silver* a yellow precipitate, both of which blacken rapidly; with *zinc-salts*, a white gelatinous precipitate.

δ. *Ethyl-compounds.*

Ethylmonosulphocarbonic Acid, $C^3H^6O^2S = (C^2H^5)HCO^2S$. (Debus, Ann. Ch. Pharm. lxxv. 130, 136, 142; lxxxii. 253.)—The potassium-salt of this acid is produced by the action of hydrate or sulphydrate of potassium on ethylic monosulphocarbonate, or of potash on ethylic disulphocarbonate (see equations, p. 495, γ). Chancel prepares it by passing carbonic anhydride into an alcoholic solution of potassic mercaptide:

$$C^2H^5KS + CO^2 = (C^2H^5)KCO^2S.$$

Ethylsulphocarbonate of potassium crystallises in long needles or shining colourless prisms, apparently isomorphous with xanthate of potassium. It is very soluble in water, but not deliquescent. Its aqueous solution decomposes gradually at ordinary temperatures, and instantly at the boiling heat, yielding ethylic carbonate, sulphide and sulphydrate, together with alcohol.

Ethylmonosulphocarbonic Sulphide, $C^6H^{10}O^4S^2 = (C^2H^5O)^2.2COS = (C^2H^5S)^2.2CO^2$. *Bicarbonate de bisulphure d'éthyle.* (Chancel, Compt. rend. xxxii. 644.)—Obtained by adding iodine to an alcoholic solution of potassic ethylmonosulphocarbonate (p. 495). It is a colourless, highly refractive oil, insoluble in water, very soluble in alcohol and ether, heavier than water; stains paper. It is decomposed by *alcoholic potash*, yielding ethylmonosulphocarbonate and sulphide of potassium, together with sulphur.—With *alcoholic ammonia*, it yields sulphur, sulphydrate, and carbonate of ammonium, together with crystals, probably consisting of ethylic carbamate (urethane).—When *ammonia-gas* is passed into its ethereal solution, crystals of sulphur are deposited, and the liquid retains in solution sulphide and allophanate of ethyl (i. 133):

$$2C^6H^{10}O^4S^2 + 4NH^3 = \underset{\substack{\text{Ethylic allo-}\\\text{phanate.}}}{2C^4H^8N^2O^3} + \underset{\substack{\text{Ethylic}\\\text{sulphide.}}}{C^4H^{10}S} + S^2 + H^2S + 2H^2O.$$

Ethylic Monosulphocarbonate, $C^5H^{10}O^2S = (C^2H^5)^2CO^2S$. (Debus, Ann. Ch. Pharm. lxxv. 136.)—Produced: 1. In small quantity by the action of ethylic chloride on ethylmonosulphocarbonate of potassium (see equations, p. 494, β).—2. In larger quantity by dry distillation of ethyldisulphocarbonic sulphide, obtained by the action of iodine on xanthate of potassium. The decomposition begins at 130°, and becomes violent at 170°; so that it becomes necessary to remove the source of heat, and leave the action to go on by itself. The first portion of the distillate thus obtained is a mixture of carbonic disulphide and ethylic monosulphocarbonate; the latter consists of ethylic disulphocarbonate, distilling at 200° (see equations, p. 494, ε). The monosulphocarbonate must be rectified till it boils constantly at 162°.

Ethylic monosulphocarbonate is a strongly refracting liquid, having a pleasant ethereal odour. Specific gravity = 1·032 at 1°. It is insoluble in water, but dissolves easily in alcohol and ether. Mixed with alcoholic *sulphydrate of potassium* and cooled to 0°, it deposits crystals of potassic ethylmonosulphocarbonate, while ethylic sulphydrate remains in solution; with alcoholic *potash*, the same products, together with alcohol and potassic carbonate (see equations, p. 495, γ). When saturated with ammonia-gas and concentrated, it yields yellow needles, mixed with a gelatinous substance.

Ethyldisulphocarbonic or **Xanthic Acid,** $C^3H^6OS^2 = (C^2H^5)HCOS^2$. (Zeise, Schw J. xxxvi. 1; xliii. 160; Pogg. Ann. xxxv. 457.—Couerbe, Ann. Ch. Phys. [2] lxi. 225.—Sacc, Ann. Ch. Pharm. li. 345.—Debus, *ibid.* lxxii. 1; lxxv. 121; lxxxii. 253.—Desains, Ann. Ch. Phys. [3] xx. 496.—Hlasiwetz, Ann. Ch. Pharm. cxxii. 87.)—The potassium-salt of this acid is produced by adding carbonic disulphide to alcoholic potash, or by the action of potassic sulphydrate on neutral ethylic disulphocarbonate (xanthic ether).

When fused hydrate of potassium is dissolved in half its weight of absolute alcohol, carbonic disulphide then slowly added till the liquid no longer exhibits an alkaline reaction, and the mixture cooled to 0°, xanthate of potassium separates in colourless needles, and an additional quantity may be obtained by evaporating the mother-liquor in a vacuum, after the excess of carbonic disulphide has been separated by water. To obtain the free acid, the potassium-salt is placed in a large cylindrical vessel, and treated with dilute sulphuric or hydrochloric acid; a milky liquid is then formed, from which the acid may be more completely separated by further addition of water.

Xanthic acid is a colourless oil, heavier than water, and insoluble therein; it has a strong odour, and its taste is acid, astringent, and bitter. It first reddens litmus, and then bleaches it. It is very inflammable, and gives off, in burning, the odour of sulphurous acid. It cannot be heated without decomposition, becoming turbid at 24°, then beginning to boil, and being resolved into alcohol and carbonic disulphide: $C^3H^6OS^2 = C^2H^6O + CS^2$. When exposed to the air, it becomes covered with a white crust. It expels carbonic acid from its alkaline salts.

The xanthates or ethyldisulphocarbonates, $\left.\begin{matrix}C^2H^5\\(CS)''\\M\end{matrix}\right\}\begin{matrix}O,\\S\end{matrix}$ are decomposed by distillation, yielding chiefly carbonic anhydride, sulphydric acid, carbonic disulphide, and a sulphuretted oil, and leaving a residue of metallic sulphide mixed with charcoal. The oil, called by Zeise *xanthogenöl*, appears to be a mixture of ethylic sulphide and sulphydrate with another sulphuretted body.

The xanthates of the alkali-metals are very soluble in water and in alcohol. The *ammonium-salt* is obtained by saturating the acid with ammonium-carbonate, or by decomposing the barium-salt with ammonium-sulphate.

Xanthate of Potassium, $(C^2H^5)KCOS^2$, is most easily prepared by adding to absolute alcohol an excess of very pure caustic potash and an excess of carbonic disulphide. The mixture immediately solidifies to a mass of interlaced silky needles, which must be washed on a filter with ether, then pressed between bibulous paper, and dried over oil of vitriol.

The salt crystallises in shining colourless prisms, which turn slightly yellow on exposure to the air. It is very soluble in water and alcohol, but insoluble in ether. Its aqueous solution decomposes when heated above 50°, yielding potassic trisulphocarbonate, alcohol, sulphydric acid, and carbonic anhydride:

$$2C^3H^5KOS^2 + 2H^2O = K^2CS^3 + 2C^2H^6O + H^2S + CO^2.$$

In the dry state, it may be heated to 200° without alteration; at higher temperatures, it gives off ethylic sulphydrate (mercaptan), sulphydric acid, water, and carbonic oxide, leaving a residue of potassic sulphide mixed with charcoal. The solution, heated with *potash*, is resolved into mercaptan and potassic ethylmonosulphocarbonate (p. 497). With *chlorine*, it yields chloride of potassium and a sulphuretted acid oil. With *iodine*, it yields ethyldisulphocarbonic sulphide, $C^6H^{10}O^2S^4$ (pp. 497, 499). Fuming nitric acid decomposes the xanthate with violence.

Xanthate of Sodium forms yellow needles.—The *barium-salt*, $C^6H^{10}Ba''O^2S^4.2H^2O$, forms very unstable laminæ, soluble in water.—The *calcium-salt* is a gummy mass.

The soluble xanthates form a white precipitate with lead-salts, yellow with cupric salts (hence the name of the acid), light-yellow with argentic and mercurous salts, the last-mentioned precipitate, however, quickly becoming brown and black.

The xanthates of the heavy metals may be obtained in the crystalline form, by decomposing a solution of sodium-ethylate in a large quantity of carbonic disulphide with the solid chlorides of the heavy metals, the mixture being kept at the boiling-point till the reaction is complete.

The liquid chlorides of antimony, arsenic, and tin, mixed with 3 pts. carbonic disulphide, are introduced into the solution of sodium-ethylate by a dropping apparatus, the action being moderated by cooling. The liquid is separated from the resulting chloride of sodium by pressure through fine linen, and the crystals obtained by its spontaneous evaporation are purified by recrystallisation from carbonic disulphide, and finally by rapid washing with ether. The antimony-, arsenic-, and iron-salts dissolve readily in carbonic disulphide, even in the cold; the chromium-, cobalt-, and nickel-salts on warming; the tin- and mercury-salts, which crystallise most quickly, require prolonged boiling to dissolve them. These salts are likewise soluble in ether and in alcohol. (Hlasiwetz.)

Xanthate of Antimony, $\left.\begin{matrix}(C^2H^5)^3\\ Sb'''\end{matrix}\right\}(COS^2)^3 = \left.\begin{matrix}(\overset{\prime\prime}{CS})^3\\ (C^2H^5)^3Sb'''\end{matrix}\right\}\begin{matrix}O^3\\ S^3\end{matrix}$, prepared as above with pentachloride of antimony, forms large, lemon-yellow, triclinic crystals, which behave like the following.—*Xanthate of Arsenic,* $(C^2H^5)^3As'''(COS^2)^3$, forms nearly colourless monoclinic tables, which melt easily, are decomposed by heat, leaving a residue of arsenious sulphide, and are decomposed by warm hydrochloric acid.—*Xanthate of Bismuth,* $(C^2H^5)^3Bi'''(COS^2)^3$, crystallises in shining golden-yellow laminæ and tables.—*Xanthate of Chromium,* $(C^2H^5)^3Cr'''(COS^2)^3$, forms shining dark-blue crystals, dissolving with violet-blue colour in carbonic disulphide.—*Xanthate of Cobalt,* $(C^2H^5)^2Co''(COS^2)^2$, forms large, well-defined, black crystals, dissolving in carbonic disulphide with dark grass-green colour. (Hlasiwetz.)

Copper-salts.—Xanthate of potassium, added to the solution of a cupric salt, forms at first a black-brown precipitate of *cupric xanthate,* which quickly changes into beautiful yellow flocks of *cuprous xanthate*. This salt is not sensibly attacked by sulphydric acid, but alkaline sulphides decompose it immediately. It is decomposed by hot hydrochloric and sulphuric acids, and strongly attacked by nitric acid. (Zeise.)

Ferric Xanthate, $(C^2H^5)^3Fe'''(COS^2)^3$, crystallises in very fine, regularly formed, monoclinic crystals, having a black colour, and dissolving in carbonic disulphide with brown-black colour. (Hlasiwetz.)

Xanthate of Lead, $(C^2H^5)^2Pb''(COS^2)^2$, prepared by adding carbonic disulphide and hydrate of lead to alcoholic potash, crystallises in colourless silky needles, very stable, insoluble in water and in ether, moderately soluble in boiling alcohol. It is slowly decomposed by sulphydric acid, immediately by sulphide of ammonium. Its solution is gradually decomposed by boiling, more quickly on addition of potash, depositing sulphide of lead. A solution of cupric sulphate poured on the crystals immediately transforms them into yellow cuprous xanthate. (Debus.)

Mercuric Xanthate, $(C^2H^5)^2Hg''(COS^2)^2$, prepared by the method of Hlasiwetz, crystallises in scales having a satiny lustre.—The *nickel-salt,* $(C^2H^5)^2Ni''(COS^2)^2$, crystallises in large, black, monoclinic tables, dissolving in carbonic disulphide with yellowish-green colour. (Hlasiwetz.)

Concentrated solutions of *silver-salts* form with soluble xanthates, a black precipitate; dilute solutions give a yellowish precipitate, which quickly blackens. (Zeise.)

Stannous Xanthate, $(C^2H^5)^2Sn''(COS^2)^2$, prepared, according to the method of Hlasiwetz, with stannic chloride, crystallises in shining golden-yellow laminæ and tables.

Ethyldisulphocarbonic Sulphide, $C^6H^{10}O^2S^4 = (C^2H^5O)^2.2CS^2$. *Aethyldioxysulphocarbonat.* (Desains, Ann. Ch. Phys. [3] xx. 469.—Debus, Ann. Ch. Pharm. lxxii.1; Jahresb. 1849, p. 419.)—Produced by the action of iodine on xanthates. If an alcoholic solution of potassic xanthate, exactly decolorised by iodine, be left to evaporate at a moderate temperature, this compound is deposited, after a few days, in lamellar crystals, which may be purified by washing with water. It may also be prepared from xanthate of lead.

Ethyldisulphocarbonic sulphide melts at the heat of the hand to a yellowish oil, insoluble in water, and having a very persistent but not unpleasant odour. It is very soluble in absolute alcohol and in ether. Its solution does not precipitate acetate of lead; when boiled with nitrate of silver, it gives a precipitate of sulphur. With mercuric chloride it forms a white precipitate, which blackens at 40°; and with platinic chloride, after a while, a brown pulverulent precipitate.

It is decomposed by heat, the decomposition commencing at about 130°, and two modes of decomposition going on simultaneously, viz.:

$$C^6H^{10}O^2S^4 = \underset{\substack{\text{Ethylic mono-}\\ \text{sulphocarbonate.}}}{C^5H^{10}O^2S} + CS^2 + S.$$

and

$$C^6H^{10}O^2S^4 = \underset{\substack{\text{Ethylic disul-}\\ \text{phocarbonate.}}}{C^5H^{10}OS^2} + CO + S^2.$$

With alcoholic *potash*, it yields a deposit of sulphur and a solution of potassic xanthate, carbonate, and sulphide:

$$C^6H^{10}O^2S^4 + 2K^2O = \underset{\text{Xanthate.}}{C^3H^5KOS^2} + \underset{\substack{\text{Ethyl-car-}\\ \text{bonate.}}}{C^3H^5KO^3} + K^2S + S.$$

$$\underset{\text{Ethyl-carbonate.}}{C^3H^5KO^3} + KHO = \underset{\text{Carbonate.}}{K^2CO^3} + \underset{\text{Alcohol.}}{C^2H^6O}.$$

With *sulphydrate of potassium*, it yields sulphur, a large quantity of sulphydric acid gas, and a solution of xanthate:

$$C^6H^{10}O^2S^4 + 2KHS = 2C^3H^5KOS^2 + H^2S + S.$$

Ammonia-gas passed into its alcoholic solution forms xanthate of ammonium and ethylic sulphocarbamate (xanthamide, p. 491):

$$C^6H^{10}O^2S^4 + NH^3 = \underset{\text{Xanthic acid.}}{C^3H^6OS^2} + \underset{\text{Xanthamide.}}{C^3H^7NOS} + S.$$

Hydrochloric acid may be distilled over ethyl-disulphocarbonic sulphide without decomposing it. *Sulphuric acid* attacks it in the cold, evolving sulphurous anhydride.

Potassium or *sodium* added to its ethereal solution mixed with a little alcohol unites rapidly with it, forming a xanthate (Drechsel, Zeitschr. f. Chem. 1865, p. 853):

$$(C^2H^5O)^2C^2S^4 + K^2 = 2(C^2H^5)KCOS^2.$$

Ethylic Disulphocarbonate or **Xanthate. Xanthic Ether.** $C^5H^{10}OS^2 = \left.\begin{matrix}C^2H^5\\(CS)''\\C^2H^5\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$. (Zeise, Ann. Ch. Pharm. lvi. 29.—Debus, *ibid.* lxxv. 121.)—Produced:—1. By the action of ethylic chloride on potassic xanthate.—2. By the dry distillation of ethyl-disulphocarbonic sulphide (p. 499). It has a pale-yellow colour, a sweetish taste, and a not very disagreeable odour; is neutral to test-paper, and has a specific gravity of 1·0703 at 18°. It boils at 200°; burns with difficulty, if not previously heated.

Xanthic ether is quite insoluble in water; *alcohol* and *ether* dissolve it in all proportions. It dissolves *iodine*, forming a brown liquid. Potassium attacks it but slightly, and only when heated. It is decomposed by strong *sulphuric acid*, and by a mixture of that acid with fuming *nitric acid*, forming oily products: it is not attacked by hydrochloric acid. Its alcoholic solution forms a white precipitate with *mercuric chloride.* It is not decomposed by mercuric oxide, or by protoxide or peroxide of lead, even when heated therewith. With an alcoholic solution of *hydrate* or *sulphydrate of potassium*, it yields mercaptan and ethylmono- or ethyl-disulphocarbonate of potassium.—When *ammonia-gas* is passed into its alcoholic solution, and the liquid then left to itself for a day, it yields a distillate of ethylic sulphide and ammonium-sulphydrate, and a residue of ethylic sulphocarbamate (xanthamide):

$$2C^5H^{10}OS^2 + 2NH^3 = H^2S + (C^2H^5)^2S + 2C^3H^7NOS.$$

Ethyl-methylic Disulphocarbonate, $C^4H^8OS^2 = (CH^3)(C^2H^5).COS^2$. (Chancel, Ann. Ch. Phys. [3] xxxv. 468.)—Obtained by distilling together 1 at. xanthate and 1 at. methylsulphate of potassium. It is a pale-yellow limpid liquid, having a specific gravity of 1·123 at 11°, a sweet taste, and a strong, ethereal, not unpleasant odour. It boils at 179°, and distils entirely without decomposition. Vapour-density = 4·652. It easily takes fire, and burns with the blue flame of sulphur, emitting large quantities of sulphurous anhydride. It is insoluble in water, but soluble in alcohol and ether. Ammonia converts it into xanthamide and methylic sulphydrate.

Ethyl-trisulphocarbonic Acid. $C^3H^6S^3 = (C^2H^5)HCS^3$. *Trisulphuretted Carbovinic Acid. Sulphoxanthic Acid.* (Chancel, Compt. rend. xxxii. 642.)—The potassium-salt of this acid, $C^3H^5KS^3$, is formed by the direct union of carbonic disulphide with sulphethylate (mercaptide) of potassium. It is a white salt, soluble in water and in alcohol; forms yellow precipitates with silver-, mercury-, and lead-salts; and with copper-salts a precipitate of a very brilliant scarlet colour, resembling mercuric iodide. These precipitates decompose quickly when heated, yielding metallic sulphides. The precipitate formed in a solution of cupric sulphate, is a cuprous salt, whose formation is accompanied by that of a persulphide, probably containing $C^6H^{10}S^6 = (C^2H^5S)^2.2CS^2$. The potassium-salt decomposes at 100° into pentasulphide of potassium, and an oil having the composition of allylic sulphide:

$$2C^3H^5KS^3 = K^2S^5 + (C^3H^5)^2S.$$

Ethylic Trisulphocarbonate. $C^5H^{10}S^3 = (C^2H^5)^2CS^3$. *Sulphocarbonate of Ethylic Sulphide.* (Schweitzer, J. pr. Chem. xxxii. 254.—Debus, Ann. Ch. Pharm. lxxv. 147.—Hüsemann, Göttinger Nachrichten, 1861, p. 275; Jahresb. 1861, p. 344.)—This ether is produced: 1. By the action of ethylic chloride or iodide on trisulphocarbonate of potassium. Vapour of ethylic chloride is passed into the red liquid precipitated on saturating an alcoholic solution of neutral potassic sulphide with carbonic disulphide; the liquid is then left at rest for a while, and the vapour again passed into it. Chloride of potassium is then gradually deposited, and on adding water to the decanted liquid, ethylic trisulphocarbonate separates as an oil, which may be purified from excess of carbonic disulphide by washing, rectification, and agitation with aqueous potash (Schweitzer).—2. Trisulphocarbonate of sodium is mixed in a long-necked flask provided with an upright condensing-tube, with an alcoholic solution of ethylic bromide or iodide. The mixture soon becomes heated to the boiling-point, and the reaction is complete in about a quarter of an hour. The ethylic trisulphocarbonate thus produced is separated from the alcoholic solution by water, then dried over chloride of calcium, and distilled till it exhibits a constant boiling-point. (Hüsemann.)

Ethylic trisulphocarbonate is a yellow oil, heavier than water, insoluble therein, very soluble in alcohol and in ether: it has a slightly alliaceous odour, and an agreeable saccharine taste, somewhat like that of anise. According to Schweitzer, it becomes red when heated, and boils between 237° and 240°. According to Hüsemann, it boils constantly at 240°. It burns with a blue flame. Alcoholic potash quickly decomposes it into trisulphocarbonate of potassium and sulphydrate of ethyl.

According to Berend (Ann. Ch. Pharm. cxxviii. 333), this ether unites directly with *bromine*, without evolution of hydrobromic acid, forming the compound $C^5H^{10}S^3Br^2$, which dissolves in ether, benzol, carbonic disulphide, and excess of bromine, and crystallises from the latter by slow evaporation in large six-sided prisms. It is decomposed by water, with formation of hydrobromic acid; potash also abstracts the bromine, reproducing the original ether. The bromine is also separated by strong nitric or sulphuric acid.

ε. *Methyl-compounds.*

Methyl-disulphocarbonic Acid. $(CH^3)HCOS^2$. *Xanthomethylic Acid.* (Dumas and Peligot, Ann. Ch. Pharm. [2] xxiv. 55.—Desains, *ibid.* [3] xx. 504.)—The *potassium-salt* of this acid, $(CH^3)KCOS^2$, obtained by adding carbonic disulphide to a solution of potash in wood-spirit, crystallises in silky fibres.—The *lead-salt* contains $(CH^3)^2Pb''C^2O^2S^4$.

The aqueous solution of the potassium-salt, treated with a solution of iodine in wood-spirit, deposits oily drops of methyl-disulphocarbonic sulphide, $C^4H^6O^2S^4 = (CH^3O)^2C^2S^4$:

$$2(CH^3)KCOS^2 + I^2 = 2KI + C^4H^6O^2S^4.$$

Methylic Disulphocarbonate, $C^3H^6OS^2 = (CH^3)^2COS^2$. *Xanthomethylic Ether.* (Cahours, Ann. Ch. Phys. [3], xix. 158.—Zeise, *ibid.* p. 123.)—When the mixture of potassic methyl-disulphocarbonate and iodine just mentioned is heated, the methyl-disulphocarbonic sulphide first formed is decomposed, sulphur and potassium-iodide being deposited, and carbonic oxide evolved; and on adding water to the mixture, methylic disulphocarbonate is deposited in the form of an oil:

$$C^4H^6O^2S^4 = (CH^3)^2COS^2 + CO + S^2.$$

This ether is a very mobile, slightly yellowish liquid, having a strong, persistent, slightly aromatic odour. It boils at 170°—172°. Specific gravity of the liquid = 1·143 at 15°; of the vapour, 4·266. With alcoholic potash, it yields methylic sulphydrate and carbonate of potassium.

Methylic Trisulphocarbonate, $(CH^3)^2CS^3$. (Cahours, Ann. Ch. Phys. [3], xix. 163.)—Obtained by distilling a mixture of the concentrated solutions of calcic methylsulphate and potassic trisulphocarbonate. It is a yellow liquid, having a strong pungent odour, nearly insoluble in water, but dissolved in all proportions by alcohol and ether. Boils at 200°—205°. Specific gravity = 1·159 at 18°. Vapour-density = 4·652. With *bromine* it forms red crystals, containing, according to Cahours, $C^3H^4Br^2S^3 = (CH^2Br)^2CS^3$; according to Berend, on the contrary (Ann. Ch. Pharm. cxxviii. 333), the methylic trisulphocarbonate unites directly with the bromine, without elimination of hydrogen.

Sulphocarbonic Ethers containing Diatomic Alcohol-radicles.

Amylenic Trisulphocarbonate, $\left.\begin{matrix}(CS)''\\(C^5H^{10})''\end{matrix}\right\}S^2$, obtained by the action of an alcoholic solution of amylenic bromide on trisulphocarbonate of sodium, is a somewhat viscid liquid, of more or less yellow-brown colour, and specific gravity = 1·073. (Hüsemann, Jahresb. 1862, p. 434.)

Ethylenic Trisulphocarbonate, $CS.C^2H^4.S^2$. (Hüsemann, Ann. Ch. Pharm.

cxxiii. 83; Jahresb. 1861, p. 651.)—Obtained by the action of alcoholic bromide of ethylene on trisulphocarbonate of sodium. It is but slightly soluble in alcohol, and separates, during the reaction, as a thick golden-yellow liquid; and by dissolving it in ether or ether-alcohol, and leaving the solution to evaporate, it is obtained in large, transparent, yellow crystals, which are combinations of a rhombic prism with a rhombic octahedron resting on the prismatic faces, and a macrodome. It has an unpleasant alliaceous odour, dissolves slowly in alcohol, better in ether-alcohol and in ether, very easily in carbonic disulphide, benzol, and chloroform. It melts at 56·5°, and when once fused, solidifies again but slowly. Specific gravity = 1·476.

Ethylenic trisulphocarbonate is converted by *ammonia* into sulphocyanate of ammonium and ethylenic sulphydrate:

$$\left.\begin{matrix}CS\\C^2H^4\end{matrix}\right\}S^2 + 2NH^3 = \left.\begin{matrix}CS\\NH^4\end{matrix}\right\}N + \left.\begin{matrix}C^2H^4\\H^2\end{matrix}\right\}S^2.$$

Heated with *sulphydrate of potassium*, it yields ethylenic sulphydrate and potassium-trisulphocarbonate. *Chlorine* acts strongly upon it, producing great heat, which causes the crystals to melt, and forming a dark-red, very fetid liquid. Moderately dilute *nitric acid* removes one-third of the sulphur, and converts the ether into ethylenic disulphocarbonate (*infra*); but fuming nitric acid heated with it as long as nitrous fumes are evolved, removes the whole of the carbon, as well as one-third of the sulphur, and converts it into ethylene-sulphurous acid, $\left.\begin{matrix}(S''O)^2\\(C^2H^4)''.H^2\end{matrix}\right\}O^4$ (Buckton and Hofmann's disulphetholic acid). See Sulphurous Ethers.

Ethylenic Disulphocarbonate or **Xanthate,** $\left.\begin{matrix}(CS)''\\(C^2H^4)''\end{matrix}\right\}\begin{matrix}O\\S\end{matrix}$. (Hüsemann, Ann. Ch. Pharm. cxxvi. 269.)—Ethylenic trisulphocarbonate, treated, as above mentioned, with moderately dilute nitric acid, yields this compound as a white crystalline mass, which, after pressure between paper, crystallises from alcohol in long thin rectangular tables. It distils in a stream of hydrogen, without decomposition; is insoluble in water, but dissolves easily in alcohol, ether, chloroform, and benzol; and separates from the last two liquids as an oil, which does not solidify till touched with the crystallised ether.

Methylenic Trisulphocarbonate, $CS.CH^2.S^2$. (Hüsemann, Ann. Ch. Pharm. cxxvi. 269; Jahresb. 1862, p. 433.)—This compound separates, on gently heating an alcoholic solution of methylenic iodide with trisulphocarbonate of sodium, as an amorphous, yellowish-white, inodorous powder, which is insoluble in water, and is converted by fuming nitric acid into methylene-sulphurous or disulphometholic acid, $(SO)^2.CH^2.H^2.O^4$.

Tritylenic or **Propylenic Trisulphocarbonate,** $CS.C^3H^6.S^2$, obtained in like manner with bromide of tritylene, is a thick brownish-yellow liquid, insoluble in water, and having an offensive odour. It has a specific gravity of 1·31 at 20°; cannot be distilled without decomposition, except in a stream of hydrogen; is converted, by moderately dilute nitric acid, into a light-yellow resinous mass; by the strong acid into tritylene-sulphurous (disulphopropolic) acid. (Hüsemann.)

Tetrylenic or **Butylenic Trisulphocarbonate,** $CS.C^4H^8.S^2$, obtained in like manner, is a more mobile liquid, having a somewhat yellowish-brown colour, and a specific gravity of 1·26 at 20°. (Hüsemann.)

SULPHOCARBOVINIC ACID. Syn. with Ethyl-disulphocarbonic or Xanthic Acid (p. 498).

SULPHOCETIC ACID. Syn. with Cetylsulphuric Acid. (See Sulphuric Ethers.)

SULPHOCHLOROBENZAMIDE. $C^7H^7ClN^2SO^3 = \left.\begin{matrix}(C^7H^3ClSO^3)''\\H^4\end{matrix}\right\}N^2 = \left.\begin{matrix}(C^7H^3ClO)''\\(SO)''\\H^4\end{matrix}\right\}\begin{matrix}N^2\\O\end{matrix}$. (R. Otto, Ann. Ch. Pharm. cxxiii. 216.)—An amide produced by the action of alcoholic ammonia on sulphochlorobenzoic chloride, $C^7H^3ClSO^3.Cl^2$. It forms yellowish crystalline grains, easily soluble in absolute alcohol and in ether.

SULPHOCHLOROBENZOIC ACID. $C^7H^5ClSO^5 = \left.\begin{matrix}(C^7H^3ClSO^3)''\\H^2\end{matrix}\right\}O^2 = \left.\begin{matrix}(C^7H^3ClO)''\\(SO)''\\H^2\end{matrix}\right\}O^3$—(Otto, *loc. cit.*)—Produced by treating monochlorobenzoic acid with phuric anhydride. The viscid mass is gently warmed with a little ordinary sulphuric acid, till, on diluting with water, only a small quantity of chlorobenzoic acid remains undecomposed. The dilute solution is neutralised with carbonate of lead, and the filtrate is evaporated; whereupon *sulphochlorobenzoate of lead*, $C^7H^3Pb''ClSO^5.3H^2O$, is at first deposited in concentric groups of silky needles, afterwards a granular mass, probably a mixture of the neutral and acid lead-salts.

Sulphochlorobenzoic acid, obtained by decomposing the lead-salt with sulphuretted hydrogen, is easily soluble in water, alcohol, and ether, and crystallises from the aqueous solution in long white hydrated needles.

The *neutral potassium-salt*, $C^7H^3K^2ClSO^5.3H^2O$, forms small needles, which dissolve readily in water and in alcohol, and give off their water at 120°.—The *acid salt*, $2C^7H^4KClSO^5.3H^2O$, crystallises from alcohol in concentric groups of needles, somewhat less soluble than the neutral salt.

The *neutral barium-salt*, $C^7H^3Ba''ClSO^5.2H^2O$, forms indistinct crusts; the *acid salt*, $C^{14}H^8Ba''Cl^2S^2O^{10}.4H^2O$, sometimes forms solid, well-developed, wavellitic crystals, sometimes granular crystals.

The *acid calcium-salt*, $C^{14}H^8Ca''Cl^2S^2O^{10}.3H^2O$, separates from hot dilute alcohol in large crystals resembling cupric sulphate.

Disulphochlorobenzoic Acid, $C^7H^5ClS^2O^8 = \left.\begin{array}{c}(C^7H^2ClO)''' \\ (SO)^2 \\ H^3\end{array}\right\}O^3$, is obtained, together with sulphochlorobenzoic acid, by heating the product of the action of sulphuric anhydride on chlorobenzoic acid for some time with ordinary sulphuric acid.

SULPHOCHOLEIC ACID. Syn. with Taurocholic Acid.

SULPHOCINNAMIC ACID. $C^9H^8SO^5 = \left.\begin{array}{c}(C^9H^6SO^3)'' \\ H^2\end{array}\right\}O^2 = \left.\begin{array}{c}(C^9H^6O)'' \\ (SO)'' \\ H^2\end{array}\right\}O^3.$

(Herzog, J. pr. Chem. xxix. 51.)—Obtained by mixing 1 pt. cinnamic acid with 8 to 12 pts. fuming sulphuric acid of specific gravity 1·92 to 1·87, saturating the diluted solution with carbonate of barium, decomposing the filtered liquid with basic acetate of lead, and treating the precipitate with sulphuretted hydrogen.

Sulphocinnamic acid remains, on evaporation in vacuo, as an amorphous slightly hygroscopic mass, very soluble in water and in alcohol. From its alcoholic solution it is deposited, by spontaneous evaporation, in elongated prisms containing $C^9H^8SO^5.3H^2O$. It precipitates the solutions of basic lead-acetate and mercurous nitrate, also that of barium-chloride after some time.

Sulphocinnamates.—Sulphocinnamic acid is dibasic, forming neutral salts, $C^9H^6M^2SO^5$, and acid salts, $C^9H^7MSO^5$, or, for diatomic metals, $C^{18}H^{14}M''S^2O^{10} = C^9H^6M''SO^5.C^9H^8SO^5$. The sulphocinnamates are for the most part very soluble in water. Those of the alkali-metals and alkaline earth-metals yield, when heated, a mixture of sulphate and sulphite, and after strong calcination, a residue from which acids eliminate sulphuretted hydrogen.

The *neutral barium-salt*, $C^9H^6Ba''SO^5.H^2O$, is nearly insoluble in water. When boiled with water acidulated with nitric acid, it deposits needles of the *acid salt*, $C^{18}H^{14}Ba''S^2O^{10}.2H^2O$. The latter is slightly soluble in water and in alcohol, permanent in the air at ordinary temperatures, but becomes dull and gives off its water at 100°. The crystals dissolve readily in dilute aqueous ammonia, and the solution, after a short time, deposits prisms, which give off water and ammonia on exposure to the air.

The *neutral potassium-salt*, $C^9H^6K^2SO^5$, obtained by double decomposition, is amorphous, and very soluble in water.—The *acid salt*, $C^9H^7KSO^5$, obtained by adding hydrochloric acid to the solution of the neutral salt, crystallises in agglomerated needles.

The *silver-salt*, $C^9H^6Ag^2SO^5$, is obtained by decomposing the barium-salt with silver-sulphate, and evaporating in a vacuum, as a grey amorphous shining crust, easily decomposed by heat.

SULPHOCUMENIC ACID. Syn. with Cumenyl-sulphurous Acid. (See Sulphurous Ethers.)

SULPHOCUMIDE. $(C^9H^{11})^2SO^2$.—This compound appears to be formed, together with cumenyl-sulphurous acid, when cumol is treated with fuming sulphuric acid, and separates, on dilution with water, as a solid body, insoluble in water, alcohol, ether, and benzol. (Beilstein and Kögler, Jahresb. 1865, p. 559.)

SULPHOCYANACETIC ACID. $C^3H^3NSO^2 = \left.\begin{array}{c}(C^2H^2O)'' \\ CN \\ H\end{array}\right\}\begin{array}{l}S \\ O.\end{array}$ Syn. with Thiocyanoglycollic Acid (*q. v.*).

SULPHOCYANIC ACID. CNHS = $\left.\begin{matrix}CN\\H\end{matrix}\right\}S$ = $\left.\begin{matrix}(CS)''\\H\end{matrix}\right\}N$. *Hydrosulphocyanic Acid. Sulphocyanhydric Acid. Sulphocarbimide.—Sulphuretted Chyazic Acid* (**Porrett**).—*Schwefelblausäure, Blutsäure, Andrazothionsäure* (**Grotthus**).—*Rhodanwasserstoffsäure* (**Berzelius**).

This acid, the sulphur-analogue of cyanic acid, was first observed by **Bucholz** in 1799 (*Beiträge zur Erweiterung und Berichtigung der Chemie*, i. 88), and by **Rink** (1804, A. Gehl. ii. 460), afterwards more distinctly recognised by **Porrett** (Phil. Trans. 1814, p. 527), determined as to its chemical constitution by **Berzelius** (Schw. J. xxxi. 42), and further examined by **Wöhler** (Gilb. Ann. lxix. 271), **Liebig** (Ann. Ch. Pharm. x. 9; xxvi. 174; xxxix. 199; l. 337; liii. 330), **Parnell** (*ibid.* xxxix. 178), **Völckel** (*ibid.* xliii. 80), and others. The metallic sulphocyanates have been analysed chiefly by **Claus** (J. pr. Chem. xv. 401) and **Meitzendorff** (Pogg. Ann. lvi. 63).

Occurrence.—Sulphocyanate of potassium or sodium occurs in very small quantity in the saliva of man, and of the sheep (**L. Gmelin**). Göbel found it in a human salivary calculus. The distilled waters of certain cruciferous plants (cochlearia, mustard, radish, &c.) give with ferric salts the characteristic reaction of sulphocyanic acid.

Formation.—Sulphocyanic acid and its salts are produced: 1. By the direct combination of cyanides with sulphur, just as cyanates are formed by the combination of cyanides with oxygen; *e.g.*, by the calcination of cyanide or ferrocyanide of potassium, &c. with sulphur, or by boiling a solution of potassic cyanide with sulphur; also by calcining azotised charcoal with potassic sulphate, or with a mixture of potassic carbonate and sulphur.

2. By the action of cyanogen-gas on monosulphides or persulphides. In the former case, a cyanide is also formed, just as the action of cyanogen on a protoxide gives rise to the formation of a cyanide and a cyanate:

$$CN + K^2S = CNK + CNKS.$$

In the case of a disulphide, the action is one of simple combination; with higher sulphides a separation of sulphur takes place; thus:

$$2CN + K^2S^2 = 2CNKS\ ;\ 2CN + K^2S^5 = 2CNKS + S^3.$$

3. By the reaction of certain cyanides with metallic persulphides; *e.g.*, mercuric cyanide and potassic trisulphide mixed in aqueous solution:

$$Hg''Cy^2 + K^2S^3 = 2CyKS + Hg''S.$$

A similar reaction is produced when Prussian-blue is boiled for a long time with potassic liver of sulphur; also when aqueous pentasulphide of potassium is mixed with hydrocyanic acid, sulphydric acid being then evolved and sulphur precipitated:

$$2HCy + K^2S^5 = 2CyKS + H^2S + S^3.$$

In like manner hydrocyanic acid, sulphur, and aqueous ammonia, to which a small quantity of ammonium-sulphydrate is added to facilitate the solution of the sulphur, yield sulphocyanate of ammonium:

$$HCy + NH^3 + S = Cy(NH^4)S.$$

A solution of hydrocyanic acid saturated with sulphydric acid, is converted, on exposure to the air, into sulphocyanic acid, in proportion as the hydrogen of the sulphydric acid is taken up by the oxygen of the air. Hence the contamination of Vauquelin's prussic acid (prepared by decomposing mercuric cyanide with sulphydric acid) with sulphocyanic acid.

4. By the action of carbonic disulphide on alcoholic ammonia, the two liquids being heated together in a sealed tube:

$$(CS)''S + NH^3 = (CS)''.H.N + H^2S.$$

5. By the decomposition of aqueous sulphocarbamic acid (p. 490):

$$\left.\begin{matrix}(CS)''\\H^3\end{matrix}\right\}\begin{matrix}N\\S\end{matrix} = \begin{matrix}(CS)''\\H\end{matrix}N + H^2S.$$

6. By the action of alkalis on ethylic sulphocarbamate (xanthamide, p. 491):

$$\left.\begin{matrix}H^2\\(CS)''\\C^2H^5\end{matrix}\right\}\begin{matrix}N\\O\end{matrix} = \left.\begin{matrix}(CS)''\\H\end{matrix}\right\}N + \left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}O.$$

These last three reactions indicate that sulphocyanic acid has the constitution of sulphocarbimide (p. 493).

7. When animal substances are charred by heating with oil of vitriol, the residue,

on being subjected to a stronger heat, yields, amongst other products, sulphocyanate of ammonium. (O. Henry, J. Chim. méd. xxi. 301.)

8. Sulphocyanic acid is formed, together with carbamide (urea), by the action of sulphydric acid on ammonio-cupric fulminate. (Gladstone, Ann. Ch. Pharm. lxvi. 1):

$$\underset{\text{Ammonio-cupric fulminate.}}{(NH^4)^2Cu''C^4N^4O^4} + 3H^2S = \underset{\text{Carbamide.}}{2CN^2H^4O} + \underset{\text{Sulphocyanic acid.}}{2CNH\overset{\bullet}{S}} + 2H^2O + Cu''S.$$

9. Sulphocyanic acid is formed in certain decompositions of volatile oil of mustard (allyl-sulphocyanic ether).

Preparation.—Sulphocyanic acid, or hydric sulphocyanate, is separated from the metallic sulphocyanates by the action of stronger acids. It may be obtained in the anhydrous state by heating dry mercurous sulphocyanate in a stream of sulphydric or hydrochloric acid gas; and in aqueous solution by the same reaction, the mercurous cyanide being suspended in water,—or by decomposing the barium-salt with an exactly equivalent quantity of sulphuric acid.

Properties.—Anhydrous sulphocyanic acid is a colourless liquid, which crystallises at 12·5° in six-sided prisms. It boils at 85° (Artus), at 102·5° (Vogel), has a pungent odour like that of acetic acid, reddens litmus strongly, and has a very acid taste. The aqueous solution exhibits similar properties.

Decompositions.—1. The anhydrous acid is very unstable, and is quickly resolved into hydrocyanic and persulphocyanic acids (iv. 378):

$$3CSHN = CHN + C^2H^2N^2S^3.$$

The aqueous solution decomposes slowly in the cold, quickly when heated, partly into carbonic dioxide, carbonic disulphide, and ammonia:

$$2CSHN + 2H^2O = CO^2 + CS^2 + 2NH^3;$$

partly into carbonic dioxide, sulphydric acid, and ammonia:

$$CSHN + 2H^2O = CO^2 + H^2S + NH^3;$$

partly also in the same manner as the anhydrous acid, yielding a solution of hydrocyanic acid and a yellow precipitate of persulphocyanic acid. In consequence of this last decomposition, sulphocyanic acid acts poisonously, like hydrocyanic acid. All these reactions are accelerated by boiling the sulphocyanic acid with concentrated acids.

Sulphocyanic acid saturated with *sulphydric acid*, yields after a while carbonic disulphide and ammonia.—With *chlorine* and *nitric acid*, it yields a yellow precipitate of persulphocyanogen (iv. 380).—Gently heated with metallic *zinc*, it gives off sulphydric acid; more slowly with iron.

Metallic Sulphocyanates. *Sulphocyanides. Rhodanides.*—Sulphocyanic acid is monobasic, forming, with monatomic metals, salts represented by the general formula $\left.\begin{matrix}CN\\M\end{matrix}\right\}S$ or $\left.\begin{matrix}(CS)''\\M\end{matrix}\right\}N$. The sulphocyanates are for the most part soluble in water and in alcohol. They are decomposed by the stronger *acids*, with elimination of sulphocyanic acid, which then generally undergoes further decomposition. Cold dilute acids, however, exert this action only on sulphocyanates corresponding to sulphides which are decomposed by the same acids: thus they do not decompose the sulphocyanates of mercury, copper, and silver.—*Nitric acid* and *chlorine* decompose the solutions of sulphocyanates, precipitating persulphocyanogen. All sulphocyanates are decomposed by *heat*, more or less strong, into nitrogen, cyanogen, carbonic disulphide, and metallic sulphide. Calcined with *potassic hydrate*, they give off carbonate of ammonium.—Sulphocyanate of potassium ignited with metallic *iron*, yields sulphide of iron and cyanide of potassium.

Soluble sulphocyanates give, with a mixture of *cupric* and *ferrous sulphates*, a white precipitate of cuprous sulphocyanate insoluble in water; they also give white precipitates with *mercurous*, *argentic*, and *auric salts*.—With *ferric salts* they give no precipitate, but a blood-red coloration, or reddish-yellow in case of very great dilution. The reaction is extremely delicate. A piece of ordinary paper held over a solution of potassic sulphocyanate mixed with concentrated hydrochloric acid, becomes reddened by the action of the evolved sulphocyanic acid on the small quantity of iron-salt contained in it. The red colour of ferric sulphocyanate may be distinguished from that of other ferric salts by two characters: 1. It is not turned yellow by addition of hydrochloric acid, even in large quantity.—2. On immersing a piece of zinc in the liquid, sulphydric acid is given off, and may be detected by its power of blackening a strip of paper impregnated with solution of lead-acetate.

SULPHOCYANATE of ALUMINIUM is a gummy mass, the solution of which is decomposed by evaporation.

Sulphocyanate of Ammonium, $NH^4CNS = NH^4CyS$.—This salt is obtained:—1. By decomposing the cupric salt with sulphydrate of ammonium, and evaporating the filtrate.—2. By mixing hydrocyanic acid with polysulphide of ammonium (a solution of sulphur in sulphydrate of ammonium), and separating the resulting sulphocyanate of ammonium from precipitated sulphur by water or alcohol. (This mode of formation is employed as a test for hydrocyanic acid, ii. 219). The prussic acid, prepared by distilling 180 pts. potassic ferrocyanide with 90 pts. strong sulphuric acid and 40 pts. water, is digested with the sulphide of ammonium obtained by saturating 60 pts. aqueous ammonia of specific gravity 0·95 with sulphydric acid, adding 60 pts. more of the ammonia-solution and 60 pts. sulphur; the mixture is boiled till the whole of the ammonium-sulphide is decomposed with precipitation of sulphur; and the liquid is filtered and evaporated. The product amounts to 40—50 pts. of dry sulphocyanate of ammonium. (Liebig.)

3. By treating carbonic disulphide with excess of ammonia:

$$CS^2 + 4NH^3 = (NH^4)CSN + (NH^4)^2S.$$

A mixture of 1500 c.c. aqueous ammonia [of what strength?] and 200 c.c. carbonic disulphide and 1500 c.c. alcohol of 86 per cent. is distilled down to one-half, after standing for 24 hours; the residual liquid is evaporated to the crystallising-point: and the sulphocyanate thus obtained is purified by one recrystallisation. The alcoholic distillate, which contains a large quantity of ammonium-sulphide, may be used for a second and even a third preparation. (Millon, J. Pharm. [3], xxxviii. 401.)

For preparation on the large scale, Gélis has patented a similar process, in which, however, the use of alcohol is avoided, and the carbonic disulphide is made to act upon a mixture of concentrated ammonia and sulphide of ammonium, the materials being mixed in the cold, and a small quantity of fixed oil (amounting to 2 or 3 per cent. of the carbonic disulphide) added, to form an emulsion with the ammonia and facilitate the admixture. An ammoniacal solution of ammonium-sulphocarbonate is thus formed, which, after separation from the layer of oil which floats on its surface (to be used in a subsequent operation), is subjected to distillation. The sulphocarbonate of ammonium is thereby resolved into sulphocyanate of ammonium and sulphydric acid:

$$(NH^4)^2CS^3 = (NH^4)CNS + 2H^2S;$$

the former remaining in the retort, while the latter passes over, together with excess of ammonium-sulphide, and may be condensed in a receiver containing aqueous ammonia, thereby supplying material for future operations.—The sulphocyanate of ammonium thus obtained is easily converted into other sulphocyanates by distillation with fixed bases. (Rép. Chim. App. 1862, p. 146; see also Sulphocyanate of Potassium, p. 513.)

4. Together with mercaptan, by the action of alcoholic ammonia on ethylic trisulphocarbonate (Hüsemann):

$$(C^2H^5)^2CS^3 + 2NH^3 = (NH^4)CNS + 2C^2H^6S.$$

Sulphocyanate of ammonium crystallises in colourless deliquescent plates, which are very soluble in water and in alcohol, melt at 147°, and decompose at a higher temperature, giving off carbonic disulphide, sulphydric acid, and ammonia, and leaving a residue of melam, which is finally converted into hydromellone. According to Liebig's formula (iii. 865, 874):

$$\underset{\text{Sulphocyanate of ammonium.}}{8(NH^4)CNS} = 2CS^2 + 4H^2S + 5NH^3 + \underset{\text{Melam.}}{C^6N^{11}H^9}.$$

and

$$\underset{\text{Melam.}}{C^6N^{11}H^9} = 2NH^3 + \underset{\text{Hydromellone.}}{C^6N^9H^3}.$$

Sulphocyanate of Barium, $Ba''Cy^2S^2.2H^2O$, crystallises in long, shining, deliquescent needles, very soluble in water and alcohol, and containing 12·4 per cent. water, which they give off between 160° and 170°.—A compound of this salt with *mercuric cyanide*, $Ba''Cy^2S^2.Hg''Cy^2$, separates in small nacreous laminæ, from a warm solution of the component salts. (Böckmann, Ann. Ch. Pharm. xxii. 153.)

Sulphocyanate of Bismuth, $Bi'''Cy^3S^3$, is a yellow powder.

Sulphocyanate of Cadmium, $Cd''Cy^2S^2$, forms shining, colourless, anhydrous crystals, slightly soluble in water. Ammonia dissolves them, and the solution yields crystals of *cadmammonium-sulphocyanate*, $(N^2H^6Cd'')''Cy^2S^2$, which are decomposed by water.

Sulphocyanate of Calcium, $Ca''Cy^2S^2.3H^2O$, forms deliquescent needles, very soluble in water and in alcohol.—The compound $Ca''Cy^2S^2.Hg''Cy^2$, obtained like the corresponding barium-salt, forms shining white laminæ. (Böckmann.)

Chromic Sulphocyanate, $Cr'''Cy^3S^3$.—Chromic hydrate dissolves easily in dilute sulphocyanic acid, forming a greenish-violet solution, which dries up over oil of vitriol to a blackish-green, amorphous, deliquescent mass. (Clasen, J. pr. Chem. xcvi. 349.)

Chromo-diammonio-sulphocyanic Acid, $N^2CrH^7Cy^4S^4 = \left.\begin{matrix}[N^2(Cr'''H^3)]'' \\ H^2\end{matrix}\right\}(CyS)^4 = \left.\begin{matrix}Cy^4 \\ Cr''' \\ H^7\end{matrix}\right\}\begin{matrix}N^2 \\ S^4\end{matrix}$. (A. Reinecke, Ann. Ch. Pharm. cxxvi. 113.)—The *ammonium-salt* of this acid, $N^2CrH^{10}Cy^4S^4 = N^2CrH^6(NH^4)Cy^4S^4$, is obtained by gradually adding pulverised dichromate of potassium to fused sulphocyanate of ammonium, till the mass becomes solid. Ammonia is then given off, with strong intumescence; and on treating the product with hot water, filtering to separate an amorphous substance, and introducing lumps of sal-ammoniac into the filtrate, the ammoniacal compound above mentioned separates in small shining scales. Its formation may be represented by the equation:

$$8(NH^4)CyS + Cr^2O^3 = 2(N^2CrH^{10}.Cy^4S^4) + 2NH^3 + 3H^2O.$$

This compound dissolves with ruby-red colour in water, alcohol, and ether, and crystallises from water in small rhombic dodecahedrons resembling garnets. It bears, without decomposition, a heat of 120°, but decomposes at a red heat, leaving sulphide of chromium; and when heated with water, yields sulphocyanate of ammonium, sulphocyanate of chromium, and chromic oxide. It is easily decomposed also by dilute acids and alkalis—in the latter case, according to the equation:

$$2(N^2CrH^{10}.Cy^4S^4) + 8KHO = 8KCyS + 6NH^3 + Cr^2O^3 + 5H^2O.$$

The same compound appears to have been obtained by Morland (Chem. Soc. Qu. J. xiii. 252), who, however, assigned to it the formula, $Cr'''Cy^3S^3.(NH^4)^2O$.

The molecule, NH^4, in the salt just described, may be replaced by other metals. The *potassium-salt*, $\left.\begin{matrix}(N^2Cr'''H^3)'' \\ H \\ K\end{matrix}\right\}Cy^4S^4$, is obtained by treating the ammonium-salt with strong potash-ley, and recrystallising from hot water. It forms ruby-coloured laminæ or cubes, dissolves with deep ruby colour in water, alcohol, and ether, and decomposes like the ammonium-salt, when boiled with water, acids, and alkalis.—The *sodium-salt*, $N^2(Cr'''H^3)HNaCy^4S^4$, prepared in like manner, crystallises in unctuous scales.—The *mercuric salt*, $N^4(Cr'''H^3)^2H^2Hg''Cy^8S^8$, is obtained, by precipitation with mercuric chloride, as a flocculent rose-coloured precipitate, insoluble in water and in dilute acids. It decomposes above 150° into sulphide of mercury and sulphide of chromium, and by boiling with potash into ammonia, sulphocyanic acid, mercuric oxide, and chromic oxide.—The *cuprous salt*, $N^2(Cr'''H^3)HCuCy^4S^4$, is obtained, by treating the ammonium-salt with cupric sulphate and sulphurous acid, as a yellow pulverulent precipitate, decomposed by heat and by potash similarly to the mercuric salt.—The ammonium-salt forms, with *nitrate of silver*, a rose-coloured precipitate quite insoluble in water and in dilute acids; and with *lead-salts*, a yellowish-red precipitate soluble in boiling water.

The *hydrogen-salt*, or free acid, is obtained, by decomposing the mercuric salt suspended in water with sulphydric acid, as a deep red solution, which is decomposed by boiling, but dries up at low temperatures to a red amorphous mass. The solution has an acid reaction, decomposes carbonates, and acquires a still darker red colour when mixed with ferric chloride.

SULPHOCYANATE OF COBALT.—Recently precipitated cobaltous hydrate dissolves in aqueous sulphocyanic acid, forming a brown-red liquid, which turns blue on concentration, and finally leaves a crystalline yellowish-brown mass, very soluble in water and in alcohol, and forming a compound with ammonia.

SULPHOCYANATES OF COPPER.—The *cupric salt*, $Cu''Cy^2S^2$, is a black crystalline powder, obtained by precipitating a concentrated solution of a cupric salt with sulphocyanate of potassium, care being taken not to add the latter in excess. The precipitate is converted by washing into a cuprous salt, and is not formed in dilute solutions. It dissolves in ammonia, and the solution yields small needles of *cuprammonium-sulphocyanate*, $(N^2H^6Cu'')''Cy^2S^2$.

The *cuprous salt*, $Cu''CyS$, is precipitated as a white powder, on adding a solution of potassium-sulphocyanate to a mixture of cupric and ferrous sulphates. It is insoluble in water and in acids, which do not decompose it, but dissolves in ammonia, forming a crystalline compound.

SULPHOCYANATES OF GOLD.—On mixing the solutions of potassium-sulphocyanate and auric chloride, a flesh-coloured precipitate is formed, soluble in ammonia.

When a solution of auric chloride neutralised with acid potassium-carbonate, is added to a solution of potassium-sulphocyanate kept in excess, a bulky orange-red precipitate is formed, consisting of *potassio-auric sulphocyanate*, $\mathrm{KAu'''Cy^4S^4 = KCyS.Au'''Cy^3S^3}$. On heating the liquid, the precipitate dissolves, and partly separates on cooling in orange-red needles of unaltered composition: the greater part, however, remains in solution, and decomposes on evaporation, with reduction of metallic gold and evolution of sulphocyanic acid, so that, finally, chloride of potassium and potassio-aurous sulphocyanate crystallise out. The precipitate of potassio-auric sulphocyanate is decomposed by water, and dissolves in alcohol and in ether. The alcoholic solution, mixed with hydrochloric acid, deposits after a while copper-red needles; soda decolorises the solution, and separates a black-blue powder; ammonia causes the formation of white needles; ferric chloride colours the solution blood-red; other metallic salts form dark-coloured precipitates.—*Potassio-aurous sulphocyanate*, $\mathrm{KAu'Cy^2S^2}$, is most readily obtained by mixing a solution of potassium-sulphocyanate, warmed to 80°, with small quantities of neutral auric chloride, as long as the red precipitate disappears on stirring. The salt, separated by evaporation and purified by recrystallisation, forms long, straw-yellow, truncated prisms, which melt at 100°, and are resolved into sulphur, carbonic disulphide, metallic gold, and sulphocyanate of potassium. The aqueous solution, mixed with hydrochloric acid, sometimes deposits copper-red needles; it forms white precipitates with ammonia, ferric chloride, mercuric chloride, argentic nitrate, and neutral plumbic acetate; yellow-brown with cupric sulphate; black-brown with stannous chloride; black with mercurous nitrate.—It is coloured red by ferrous sulphate, with precipitation of gold; brown by sulphydric acid; it blackens slowly on exposure to light.—The precipitate formed by ammonia, $\mathrm{NH^3.AuCyS}$, gradually decomposes and turns black; hot water abstracts ammonia from it, leaving a green powder. (P. T. Cleve, Kongl. Vetenskap. Akad. Förhandlingar, xx. 233; Jahresb. 1855, p. 295.)

SULPHOCYANATES OF IRON.—The *ferrous salt* is soluble, of pale-green colour, and very unstable.

The *ferric salt* is blood-red, nearly black, deliquescent, soluble in water and in alcohol. The blood-red colour of this salt is produced whenever a sulphocyanate is mixed with a ferric salt. It is destroyed by alkalis which precipitate ferric oxide; also by many acids (*e.g.* phosphoric, arsenic, iodic, oxalic), even in small quantity; but restored by addition of a ferric salt; hydrochloric acid, even when concentrated, does not decolorise the liquid; nitric acid, on the other hand, decomposes the sulphocyanate, and destroys the colour (p. 505).

SULPHOCYANATES OF LEAD.—The *neutral salt*, $\mathrm{Pb''Cy^2S^2}$. is gradually deposited in opaque shining-yellow crystals, on mixing a solution of lead-acetate with sulphocyanate of potassium. The crystals are monoclinic, exhibiting the dominant combination, $+P\ .\ -3P.\ oP\ .\ \infty P2\ .\ +3P\infty$. Angle $\infty P2 : \infty P2$ (clinod.) = 120° 38′; $oP : \infty P2$ = 111° 31′; $oP : +P$ = 116° 55′; $oP : -3P$ = 119° 3′; $oP : 3P\infty$ = 87° 45′. Axes, $a : b : c = 0{\cdot}923 : 1{\cdot}1162 : 1$. Angle $b : c$ = 65° 20′. Specific gravity of crystals = 3·82. The salt is but slowly decomposed by sulphydric acid. It is insoluble in water, but boiling water converts it into a *basic salt*, $\mathrm{Pb''Cy^2S^2.Pb''H^2O^2}$. The latter is likewise obtained on mixing sulphocyanate of potassium with ammoniacal plumbic acetate, or with the basic acetate, as a white curdy precipitate, becoming yellowish and pulverulent when dry.

SULPHOCYANATE OF MAGNESIUM, $\mathrm{Mg''Cy^2S^2.4H^2O}$.—Confused crystals, very soluble in water and in alcohol. The compound $\mathrm{Mg''Cy^2S^2.Hg''Cy^2}$, prepared like the corresponding barium-salt, is a white crystalline powder. (Böckmann.)

SULPHOCYANATE OF MANGANESE.—Very soluble.

SULPHOCYANATES OF MERCURY.—The *mercurous salt*, $\mathrm{Hg'CyS}$, is a white precipitate, formed on mixing mercurous nitrate with sulphocyanate of potassium (Wöhler); according to Claus, the solutions should be very dilute. The dry precipitate swells up suddenly when heated, giving off nitrogen, carbonic disulphide, and vapour of mercury, and leaving a grey mass resembling graphite, which by calcination is converted into mellone. On account of this property, the salt is used for the preparation of the toys called "Pharaoh's serpents." It is resolved by boiling water into metallic mercury and mercuric sulphocyanate.

The *mercuric salt*, $\mathrm{Hg''Cy^2S^2}$, is obtained as a white precipitate, composed of anhydrous needles, on mixing mercuric chloride with sulphocyanate of potassium; it is very slightly soluble in water, moderately soluble in alcohol (Crookes). A solution of mercuric oxide in sulphocyanic acid yields, by evaporation, needles containing water (Berzelius).—An *oxysulphocyanate*, $\mathrm{Hg''Cy^2S^2.2Hg''O}$, is obtained, by adding ammonia to the solution of mercuric sulphocyanate, as a lemon-yellow powder, which decomposes quickly at 180°, and leaves mellone when calcined.

Mercuric sulphocyanate forms several double salts, which have been examined chiefly by Cleve (Kongl. Vetenskap. Akad. Förhandlingar, xxii. 9; J. pr. Chem. xci. 227). —The *cobalt-salt*, $\mathrm{Hg''Co''Cy^4S^4 = Hg''Cy^2S^2.Co''Cy^2S^2}$, is formed by direct union of its component salts, or by gradually adding mercuric cyanide to a solution of cobaltous sulphocyanate acidulated with sulphocyanic acid, separates in indigo-blue four-sided prisms, permanent in the air, slightly soluble in water and in dilute hydrochloric acid, easily in nitric acid. The same compound is sometimes also formed (together with the yellow salt, $\mathrm{Hg''Cy^2.Co''Cy^2S^2.4H^2O}$), on mixing mercuric cyanide with sulphocyanate of cobalt.—The *ferrous salt*, $\mathrm{Hg''Fe''Cy^4S^4}$, separates, from a mixture of mercuric sulphocyanate and ferrous chloride left for some time in a vacuum, as a brown crystalline powder, permanent in the air.—The *nickel-salt*, $\mathrm{Hg''Ni''Cy^4S^4.2H^2O}$, separates from a mixture of the component salts, in small sky-blue needles, which dissolve readily in hot water, and give off their water of crystallisation at 120°. *Zinc-mercuric sulphocyanate*, $\mathrm{Hg''Zn''Cy^4S^4}$, is formed, on mixing mercuric sulphocyanate with a zinc-salt, as a white precipitate, nearly insoluble in cold water. (Cleve.)

A *potassio-mercuric sulphocyanate*, $\mathrm{Hg''KCy^3S^3 = Hg''Cy^2S^2.KCyS}$, is prepared by triturating mercurous chloride with a strong solution of potassium-sulphocyanate. The liquid, filtered from the black magma thus produced, yields by evaporation a mixture of yellow tables, cubes, and octahedrons, easily separated by mechanical selection. The yellow tables, which constitute the potassio-mercuric sulphocyanate, are purified by crystallisation from boiling alcohol; whence the salt separates in radiate groups of white nacreous needles. It dissolves sparingly in cold, more easily in hot water; very easily in aqueous chloride of ammonium or potassium; easily in alcohol, especially at the boiling heat; also in ether. Ammonia added to the aqueous solution throws down the oxysulphocyanate above described. (Claus, J. pr. Chem. xv. 407.)

SULPHOCYANATE OF NICKEL is obtained, as a yellow crystalline powder, by evaporating the green solution of nickel-oxide in sulphocyanic acid. It dissolves in ammonia, forming a blue liquid, which yields blue efflorescent crystals, $\mathrm{(N^2H^6Ni')Cy^2S^2.2NH^3}$, decomposible by water.

SULPHOCYANATE OF PALLADIUM is easily soluble in water.

SULPHOCYANATES OF PLATINUM.—*Platinic sulphocyanate* does not appear to be known in the separate state.—The *platinous salt*, $\mathrm{Pt''Cy^2S^2}$, probably constitutes the red or brown non-crystalline substance obtained by decomposing one of the following double salts with chlorine or nitric acid; *e.g.*, with chlorine and sulphocyanate of potassium:

$$\mathrm{K^2Pt^{iv}Cy^6S^6 + 11Cl^2 + 16H^2O = Pt''Cy^2S^2 + 2KHSO^4 + 2H^2SO^4 + 22HCl + 4HCy.}$$

It is insoluble in water and in alcohol, is not attacked by potash, but is coloured yellow by ammonia. It gave by analysis 8·53 and 8·72 per cent. carbon, 9·92 nitrogen, 18·77 sulphur, 62·27 and 62·02 platinum, besides 0·39 and 1·5 hydrogen, the formula $\mathrm{PtCy^2S^2}$ requiring 7·64 carbon, 8·93 nitrogen, 20·38 sulphur, and 63·05 platinum.

Double Salts of the Platinum-sulphocyanates. (G. B. Buckton, Chem. Soc. Qu. J. vii. 22.)—The sulphocyanates of platinum form two series of double salts, called sulphocyanoplatinites and sulphocyanoplatinates, analogous to the chloroplatinites and chloroplatinates, and represented by the following general formulæ, M denoting a monatomic, and N a diatomic, metal:

$$\text{Sulphocyanoplatinites . . . } \left.\begin{matrix}\mathrm{M^2}\\ \mathrm{N''}\end{matrix}\right\}\mathrm{Pt''Cy^4S^4} = \left.\begin{matrix}\mathrm{2MCyS}\\ \mathrm{N''Cy^2S^2}\end{matrix}\right\}\mathrm{Pt''Cy^2S^2}.$$

$$\text{Sulphocyanoplatinates . . . } \left.\begin{matrix}\mathrm{M^2}\\ \mathrm{N''}\end{matrix}\right\}\mathrm{Pt^{iv}Cy^6S^6} = \left.\begin{matrix}\mathrm{2MCyS}\\ \mathrm{N''Cy^2S^2}\end{matrix}\right\}\mathrm{Pt^{iv}Cy^4S^4}.$$

The potassium-salts are formed by the action of potassic sulphocyanate on platinous and platinic chloride respectively. The salts of the alkali-metals and alkaline earth-metals are soluble in water; those of the heavy metals are insoluble, and are formed by double decomposition. All these salts are strongly coloured, exhibiting various shades of colour, from light-yellow to dark-red. They are quickly decomposed by heat, emitting a peculiar odour. Ammonia attacks the salts of both series, forming sulphocyanate of platosammonium (p. 513). Their decomposition by chlorine and by nitric acid has been mentioned above.

The following table exhibits the reactions of the soluble salts of the two series with various metallic solutions:—

Reagents.	Sulphocyanoplatinites.	Sulphocyanoplatinates.
Neutral Lead-salts	No change	Soluble golden laminæ
Basic Lead-salts	Pale-yellow precipitate	Fine red precipitate
Ferrous salts	No change	Black shining grains
Cobalt-salts	No change	Orange-red precipitate
Cuprous salts	Purplish-black precipitate	Rich brown precipitate
Cupric salts	Purplish-black precipitate	Brick-red precipitate
Mercurous salts	No precipitate: liquid changes colour when heated	Orange precipitate
Silver-salts	Pale-yellow precipitate	Red or orange precipitate
Auric salts	Salmon-coloured precipitate	Salmon-coloured precipitate
Salts of Platosamine	Fine yellow precipitate	Copious orange precipitate
Salts of Diplatosamine	Flesh-coloured precipitate	Fine vermilion-red precipitate
Chromic acid	Copious reddish precipitate, with evolution of hydrocyanic acid	No precipitate
Ferrocyanide of Potassium	Nearly white precipitate on boiling	Prussian-blue formed on boiling

1. *Sulphocyanoplatinites*, $M^2Pt''(CyS^2)^4$.

Hydric Sulphocyanoplatinite or *Sulphocyanoplatinous Acid*, $H^2Pt''Cy^4S^4$.—Obtained by cautiously decomposing sulphocyanoplatinite of barium with dilute sulphuric acid. The aqueous solution is speedily decomposed by evaporation, even in vacuo, the sulphur being oxidised at the expense of the water. The chief products of the decomposition are sulphocyanic acid and a red or yellow deposit rich in platinum.

Sulphocyanoplatinite of Potassium.—Obtained: 1. By dissolving platinous chloride in sulphocyanate of potassium, the solution being attended with considerable rise of temperature.—2. Better, by the action of sulphocyanate of potassium on chloroplatinate of potassium, the sulphocyanate being in excess. As sulphocyanoplatinite of potassium is extremely soluble, and does not crystallise well by evaporation, it is best to use the sulphocyanate of potassium in the form of a concentrated solution, and to add the platinum-salt by small quantities at a time, so as to avoid too great a rise of temperature. The liquid on cooling deposits a mass of small needles, which must be purified from chloride of potassium by solution in strong alcohol, from which again the salt is best recovered by spontaneous evaporation. The crystals are then pressed between paper to remove the excess of sulphocyanate of potassium, and the salt once more crystallised from an aqueous solution.

It forms stellar groups of crystals, which when examined by the microscope appear like six-sided prisms of a fine red colour. They dissolve readily in 2½ pts. of water at 15·5°, and are soluble to any extent in warm alcohol. The solution of the pure salt is orange-red; a port-wine colour denotes impurity. The crystals are not deliquescent, and when perfectly dry, do not appear to be affected by a temperature of 100°. The salt is decomposed by ammonia, yielding sulphocyanate of platosammonium which crystallises out, and sulphocyanate of potassium which remains in solution.

Sulphocyanoplatinite of Silver, $Ag^2Pt''Cy^4S^4$.—Curdy precipitate, somewhat resembling sulphocyanate of silver, partially soluble in ammonia, with decomposition. It dissolves in sulphocyanate of potassium, but the solution is decomposed by water.

Tetrammonioplatinous Sulphocyanoplatinite, $\left.\begin{matrix}(N^4H^{12}Pt'')''Cy^2S^2\\ Pt''Cy^2S^2\end{matrix}\right\}$, or *Sulphocyanoplatinite of Diammo-platoso-diammonium*, $\left.\begin{matrix}[N^2H^4(NH^4)^2Pt'']''\\ Pt''\end{matrix}\right\}Cy^4S^4$.—Obtained, as a bulky flesh-coloured precipitate, by decomposing the chloride of diplatosammonium with a soluble sulphocyanoplatinite.—Heated on platinum-foil, it gives off ammoniacal gas, fuses into a black bubbling mass, and then burns like tinder, leaving bright spongy platinum. It is quite insoluble in water and in alcohol, but dilute hydrochloric acid dissolves it rather freely. It is polymeric with sulphocyanate of platosammonium (p. 513).

2. *Sulphocyanoplatinates.*

Sulphocyanoplatinic Acid, $H^2Pt^{iv}Cy^6S^6$.—Obtained by precipitating a warm and concentrated solution of the lead-salt with sulphuric acid. The filtered liquid is of a deep-red colour, and has a strongly acid taste. It displaces carbonic acid from its alkaline salts, and dissolves metallic zinc, with evolution of hydrogen, and production of a yellow insoluble substance. When rapidly evaporated in vacuo, it leaves a confused semi-crystalline mass. When concentrated over the water-bath, it is quickly decomposed, leaving a brown amorphous mass, rich in platinum. On distilling it at a gentle heat, an acid liquid passes over, containing hydrocyanic and sulphocyanic acids. It combines directly with bases.

Sulphocyanoplatinate of Ammonium.—The acid does not combine rapidly with free ammonia; but the salt is easily prepared by boiling 1 pt. of ammonium-sulphate for a few minutes in a strong solution of 3·5 pts. potassic sulphocyanoplatinate; it may be separated, after cooling, from the sulphates of ammonium and potassium, by means of alcohol, and purified by recrystallisation from hot water. It crystallises in hexagonal plates of a fine crimson colour. It is stable at ordinary temperatures, but gives off the odour of sulphocyanic acid when its aqueous solution is boiled.

Sulphocyanoplatinate of Potassium.—Prepared: 1. By the action of potassic sulphocyanate on platinic chloride. When platinic chloride is added to a cold solution of potassic sulphocyanate, a precipitate of potassic chloroplatinate is formed, with evolution of sulphocyanic acid. But if the platinic chloride be poured into a strong solution of the sulphocyanate previously heated to 70° or 80°, no precipitate is formed; but the liquor acquires a deep-red colour, and on cooling deposits beautiful laminæ of potassic sulphocyanoplatinate. This process involves a considerable waste of potassic sulphocyanate, in consequence of the presence of free hydrochloric acid, which likewise, if the temperature rises above a certain point, decomposes the product, forming a brown flocculent precipitate (platinous sulphocyanate).

2. Better: a solution of 4 pts. chloroplatinate of potassium is added to a solution of 5 pts. pure sulphocyanate of potassium (weighed in the fused state) in a moderate quantity of water, and the mixture is heated nearly to the boiling-point:

$$K^2Pt^{iv}Cl^6 + 6KCyS = K^2Pt^{iv}Cy^6S^6 + 6KCl.$$

A deficiency of the sulphocyanate must be avoided, as in that case an insoluble brown substance is formed, which renders the purification of the crystals very difficult. The filtered liquid, on cooling, deposits the sulphocyanoplatinate in beautiful crystals, often of large size. To remove traces of chloride of potassium, the crystals may be redissolved in boiling alcohol, and the solution passed through a filter surrounded with hot water, to prevent too rapid crystallisation.

Sulphocyanoplatinate of potassium forms six-sided prisms or laminæ, of a deep carmine colour and very nauseous taste. The aqueous solution yields the salt in hexagonal plates, but from the alcoholic solution it is often deposited in double six-sided pyramids united base to base, and with truncated summits. Permanent in the air at ordinary temperatures. It dissolves in 12 pts. water at 60°, much more freely in boiling water, and still more in boiling alcohol. The solutions have a deep-red colour, becoming yellow when very dilute. One drop of the saturated solution gives a distinct yellow tinge to a gallon of water.

Decompositions.—1. Sulphocyanoplatinate of potassium is decomposed at a red heat, yielding sulphocyanate of potassium, gaseous products, and reduced platinum.—2. When gently heated in contact with the air, it burns with a blue sulphurous flame and peculiar odour.—3. Sulphuric acid converts it into sulphocyanic acid, suphocyanate of potassium, and platinic sulphide:

$$K^2Pt^{iv}Cy^6S^6 + 2H^2S = PtS^2 + 2KCyS + 4HCyS.$$

Similarly, with sulphide of ammonium:

$$K^2Pt^{iv}Cy^6S^6 + 2(NH^4)^2S = PtS^2 + 2KCyS + 4NH^4CyS.$$

4. The salt is decomposed by strong sulphuric and hydrochloric acid. Nitric acid and chlorine likewise decompose it, yielding platinous sulphocyanate, $Pt''Cy^2S^2$, and other products (p. 509).—5. Ammonia and carbonate of ammonia added to a saturated solution of the salt, quickly decompose it, changing the colour to pale-yellow in a few minutes, and precipitating *sulphocyanate of platosammonium*, in fine yellow needles, the liquid retaining in solution sulphate and sulphocyanate of potassium, together with sulphocyanate and cyanide of ammonium:

$$3K^2Pt^{iv}Cy^6S^6 + 8NH^3 + 4H^2O = 3(N^2H^6Pt'')''Cy^2S^2 + K^2SO^4 + 4KCyS + \\ 2NH^4CyS + 5HCyS + HCy.$$

6. Potash converts the salt into a red gelatinous mass, without evolution of ammonia.—7. When it is gently heated with carbonate of potassium, carbonic anhydride is evolved; the mixture becomes partially decolorised; sulphocyanoplatinite of

potassium is deposited, and the liquid retains in solution sulphate, sulphocyanate of potassium, and cyanide of potassium:

$$\mathrm{3K^2Pt^{iv}Cy^6S^6 + 4K^2CO^3 = 3K^2Pt''Cy^4S^4 + K^2SO^4 + 5KCyS + KCy + 4CO^2.}$$

—8. A pure solution of potassic sulphocyanoplatinate does not produce a blood-red colour with ferric salts; but the mixture becomes nearly black and opaque when heated, from formation of a substance which separates in heavy lustrous grains.

Sulphocyanoplatinate of Sodium, obtained by precipitating the lead-salt with sulphate of sodium, crystallises readily in broad garnet-coloured tables, soluble in water and in alcohol.

Sulphocyanoplatinate of Barium.—Prepared by dissolving 3 pts. of the dry potassium-salt in an aqueous solution of 1 pt. of chloride of barium (or, as an excess of the latter is desirable, 9 pts. $\mathrm{K^2PtCy^6S^6}$ to 4 pts. $\mathrm{BaCl^2}$), evaporating the solution, and extracting with alcohol.—Crystallises in long flattened prisms of a deep-red colour, and often of considerable size. Not so stable as the potassium-salt.

Cupric Sulphocyanoplatinate.—Precipitated on mixing a solution of the potassium-salt with cupric sulphate. Exhibits a brick-dust colour when first precipitated, but changes at a boiling heat to a black insoluble powder. Forms a fine green solution with ammonia, but on the addition of hydrochloric acid, the copper-salt is reproduced, with dark-brown colour.

Sulphocyanoplatinates of Iron.—*a. Ferrous salt*, $\mathrm{Fe''Pt^{iv}Cy^6S^6}$.—Obtained by adding a slightly acidulated solution of ferrous sulphate to a concentrated solution of potassic sulphocyanoplatinate. Black crystalline precipitate, which, when examined by the microscope, is seen to be composed of shining six-sided laminæ with rounded edges. It is not affected by dilute sulphuric, hydrochloric, or nitric acid; but strong nitric acid dissolves it, with formation of sulphuric acid. Cold solution of potash converts it into ferric oxide and a yellow liquid containing platinum and sulphocyanic acid. It is insoluble in water and in alcohol.

β. Ferric Salt.—Prepared in like manner with ferrous salt, but not precipitated till the mixture is boiled. Resembles the ferrous salt.

Sulphocyanoplatinates of Lead.—*a. Neutral*, $\mathrm{Pb''Pt^{iv}Cy^6S^6}$.—Precipitated in the form of brilliant golden hexagonal plates, on mixing the concentrated solutions of neutral acetate of lead and sulphocyanoplatinate of potassium. Soluble in alcohol; less soluble in cold water, with which it may be washed; cannot be crystallised from hot water without decomposition.

β. Basic, $\mathrm{Pb''O.Pb''Pt^{iv}Cy^6S^6}$.—Obtained as a brilliant red precipitate, on mixing the concentrated solutions of potassic sulphocyanoplatinate and basic lead-acetate. Insoluble in water; readily soluble in dilute nitric and in acetic acid.

Mercurous Sulphocyanoplatinate, $\mathrm{Hg^2Pt^{iv}Cy^6S^6}$.—Heavy curdy precipitate, obtained by adding mercurous nitrate to sulphocyanoplatinate of potassium. Its colour is deep orange at first, but changes to a pale primrose-yellow when the liquid is heated to the boiling-point. In the dry state, it bears a considerable degree of heat without alteration. Heated in the air-bath to between 140° and 150°, it suddenly swells up into a substance having a peculiar metallic and arborescent appearance, somewhat like coarse tea, and emits a jet of spontaneously inflammable gas. No further change is observed till the temperature rises to 250°; but at a heat below redness, mercurial vapours and cyanogen-gas are liberated; and finally the mass, if exposed in an open crucible, burns away like tinder, leaving a residue of platinum. The salt, when subjected to dry distillation, in a retort, yields a mixture of nitrogen-gas and vapour of carbonic disulphide.

Sulphocyanoplatinate of Silver, $\mathrm{Ag^2Pt^{iv}Cy^6S^6}$.—Prepared by decomposing a solution of the potassium-salt with nitrate of silver. Heavy, curdy, deep orange-coloured precipitate, which shrinks and agglutinates into a tenacious mass when boiled with water, but hardens again on boiling. The dry salt, when gently heated, swells up considerably, and if in contact with the air, takes fire and burns with a blue flame. Before the blowpipe, it fuses into a metallic bead of silver and platinum.—Nitric acid decomposes it rapidly, with formation of sulphuric acid, evolution of nitric oxide, and precipitation of a yellow substance.—When recently precipitated, it dissolves in cold aqueous ammonia, but the solution decomposes at a higher temperature. The salt is decomposed by hot caustic potash, yielding sulphocyanate of potassium, platinic oxide, and oxide of silver:

$$\mathrm{Ag\,Pt^{iv}Cy^6S^6 + 6KHO = 6KCyS + PtO^2 + Ag^2O + 3H^2O.}$$

It dissolves in sulphocyanate of potassium, but, on adding water to the liquid, sulphocyanate of silver is precipitated, and sulphocyanoplatinate of potassium remains in solution:

$$\mathrm{Ag^2Pt^{iv}Cy^6S^6 + 2KCyS = 2AgCyS + K^2Pt^{iv}Cy^6S^6.}$$

Sulphocyanate of Platosammonium, $C^2H^6N^4S^2Pt = N^2H^6Pt''.Cy^2S^2$.—This salt, polymeric and metameric with tetrammonioplatinous sulphocyanoplatinite (p. 510), is obtained: 1. By the action of ammonia on sulphocyanoplatinite of potassium:

$$K^2Pt''Cy^4S^4 + 2NH^3 = N^2H^6Pt''.Cy^2S^2 + 2KCyS.$$

2. By the action of ammonia, or its carbonate, on sulphocyanoplatinate of potassium (see p. 511). Caustic ammonia acts more quickly than the carbonate, but must not be used in the concentrated state, as the product is then contaminated with an insoluble substance. The crystals are collected on a filter, washed with cold water, and recrystallised from hot alcohol.—3. By double decomposition with sulphocyanate of potassium and chloride of platosammonium:

$$N^2H^6Pt''Cl^2 + 2KCyS = N^2H^6Pt''.Cy^2S^2 + 2KCl.$$

One part of sulphocyanate of potassium and 1·6 pt. chloride of platosammonium are dissolved together in water; the mixture heated nearly to its boiling-point; an equal volume of alcohol added, to increase the solubility of the product; and the liquid filtered hot. Sulphocyanate of platosammonium is then deposited in crystals, on cooling.

This salt forms straw-yellow needles, which, when examined by the microscope, appear to be rhomboïdal prisms. Melts between 100° and 110°, to a clear garnet-coloured syrup, which hardens again as it cools. It dissolves sparingly in cold water, more readily in alcohol. It decomposes at 180°, giving off ammonia and hydrocyanic acid; and if exposed to the air, evolves also sulphurous anhydride and leaves metallic platinum; no sulphide of carbon is given off. It is not attacked by hydrochloric or by dilute sulphuric acid. The aqueous solution produces no change in salts of copper, lead, or mercury; but when added to a solution of sulphate or nitrate of silver, it forms a light-yellow precipitate containing platinum. When boiled, it gives off ammonia, and deposits the yellow insoluble matter above mentioned; the same effect appears to be produced by caustic potash.

Sulphocyanate of Potassium, $CNKS = KCyS$.—This salt is prepared: 1. By fusing cyanide of potassium with sulphur, or 2 pts. of the ferrocyanide with 1 pt. sulphur; or by fusing 17 pts. of potassic carbonate with 32 pts. sulphur, and adding 46 pts of dry potassic ferrocyanide. The heat must be continued till the melted mass gives off bubbles, which burn in the air with a red flame; and it must be carefully regulated, as if it is insufficient, part of the ferrocyanide will remain undecomposed; and if it be too much raised, part of the resulting sulphocyanate will be converted into mellanide. The fused mass, when cold, is dissolved in water; the iron contained in the solution is precipitated by carbonate of potassium; the filtrate is evaporated to dryness; the residue digested with alcohol, and the alcoholic solution left to evaporate. To avoid the use of alcohol, **Meillet** (J. Pharm. xxvii. 628) neutralises the filtrate separated from the iron precipitate with acetic acid, evaporates, and purifies the sulphocyanate by crystallisation.—2. Sulphocyanate of potassium may also be prepared, in the same manner as the sodium-salt, by fusing 1 pt. of anhydrous potassic ferrocyanide with 3 pts. of the anhydrous hyposulphite (**Fröhde**).—3. Gelis prepares sulphocyanate of potassium on the large scale by heating sulphocyanate of ammonium with potash, or sulphocarbonate of ammonium with sulphide of potassium (p. 506):

$$2(NH^4)^2CS^3 + K^2S = 2KCNS + 2(NH^4)HS + 3H^2S.$$

Sulphocyanate of potassium crystallises in long striated prisms, or in needles with four-sided summits, very much like saltpetre. They are anhydrous, and have a specific gravity of 1·866—1·906 (**Bödeker**). The salt is very deliquescent, fusible, and very soluble in boiling alcohol. It has a cooling pungent taste, somewhat like that of radishes, and is poisonous.

The aqueous solution of potassic sulphocyanate decomposes, with evolution of ammonia, gradually at ordinary temperatures, more quickly at the boiling heat. The alcoholic solution is more stable. The concentrated solution dissolves recently precipitated *argentic cyanide*, which is thrown down from it in the crystalline state on dilution. It likewise dissolves a considerable quantity of recently precipitated *argentic chloride*, also of *argentic sulphocyanate*, forming therewith a crystalline compound.

Sulphocyanate of potassium, when melted in close vessels, bears a dull red heat without decomposition, but when calcined in contact with the air, it yields sulphate; if the salt is moist, sulphide of potassium is obtained, with evolution of ammonium-carbonate.

When dry *chlorine* is passed into melted sulphocyanate of potassium, chloride of sulphur is given off, together with solid chloride of cyanogen, which sublimes in needles. At a certain stage of the decomposition, a thick red vapour is evolved, which condenses into a red or yellowish-red sublimate containing 67·9 per cent. sulphur; and a residue is left, consisting, according to Liebig, of chloride of potassium and impure mellone. According to Völckel (Pogg. Ann. lviii. 152), neither the red sublimate nor the mellone is produced if the chlorine is quite dry and free from hydrochloric acid. Chlorine passed into an aqueous solution of the sulphocyanate, not too dilute, throws down an orange-coloured precipitate of persulphocyanogen (iv. 380). An alcoholic solution of *iodine* is not decolorised by an alcoholic solution of potassic sulphocyanate, even at the boiling heat.

Strong *nitric acid* added to the aqueous solution throws down persulphocyanogen. Dilute nitric acid, nitrous acid, and other oxidising agents, also impart to the solution a deep but transient blood-red colour, which is distinguished from that produced by ferric salts by its greater instability. (Jahresb. 1852, p. 429; 1857, p. 237; 1865, p. 294.)

Permanganate of potassium, peroxide of manganese, and peroxide of lead, oxidise only the sulphur of the sulphocyanate, converting it into sulphuric acid, the formation of which is probably preceded by that of a cyanogen-compound containing a smaller proportion of sulphur than the sulphocyanate. (Hadow, Chem. Soc. Qu. J. xi. 174.)

When dry *hydrochloric acid* is passed over fused sulphocyanate of potassium, great heat is produced; hydrocyanic acid, carbonic disulphide, and sal-ammoniac are given off; and a thick yellowish-red sublimate is formed, which, when exposed to moist air, gives off acid vapours capable of reddening ferric salts. (Liebig.)

Sulphocyanate of potassium gently heated with *pentachloride of phosphorus*, yields gaseous chloride of cyanogen, phosphoric sulphochloride, and chloride of potassium:

$$\mathrm{KCyS} + \mathrm{PCl^5} = \mathrm{CyCl} + \mathrm{KCl} + \mathrm{PSCl^3}.$$

At a higher temperature other products are formed. (Schiff, Ann. Ch. Pharm. cvi. 116.)

An aqueous solution of potassic sulphocyanate yields, by *electrolysis*, sulphuric acid, sulphurous acid, hydrocyanic acid, and sulphur. (Schlagdenhauffen, J. Pharm. [3], xlix. 100.)

Dry sulphocyanate of potassium heated with metallic iron is converted into ferrocyanide of potassium, together with ferrous and potassic sulphides:

$$6\mathrm{KCyS} + \mathrm{Fe^6} = \mathrm{K^4Fe''Cy^6} + 5\mathrm{Fe''S} + \mathrm{K^2S}.$$

This process is applied by Gelis to the manufacture of the ferrocyanide. (See Rép. Chim. App. 1862, p. 370; Richardson and Watts's *Chemical Technology*, [5], i. 399.)

SULPHOCYANATE OF SILVER, AgCyS.—White curdy precipitate, insoluble in water but soluble in ammonia, whence it crystallises in shining scales free from ammonia. Dry chlorine free from hydrochloric acid, converts it into solid chloride of cyanogen, chloride of sulphur, and chloride of silver; with moist acid chlorine, it yields also a red sublimate. It dissolves easily in aqueous sulphocyanate of potassium, and the saturated solution left over sulphuric acid, deposits rhomboïdal octahedrons of the double salt KCyS.AgCyS, which is completely decomposed by water, melts without decomposition at 140°, but decomposes at a higher temperature.

SULPHOCYANATE OF SODIUM, NaCyS.—This salt may be produced in the same manner as sulphocyanate of potassium, also by fusing cyanide or ferrocyanide of potassium with hyposulphite of sodium:

$$4\mathrm{KCy} + 4\mathrm{Na^2S^2O^3} = 4\mathrm{NaCyS} + 2\mathrm{K^2SO^4} + \mathrm{Na^2SO^4} + \mathrm{Na^2S};$$
$$2\mathrm{K^4Fe''Cy^6} + 12\mathrm{Na^2S^2O^3} = 12\mathrm{NaCyS} + 4\mathrm{K^2SO^4} + 5\mathrm{Na^2SO^4} + \mathrm{Na^2S} + 2\mathrm{Fe''S}.$$

A convenient mode of preparation is to heat 1 pt. of potassic ferrocyanide with 3½ pts. anhydrous sodic hyposulphite in a porcelain dish, till the hyposulphurous acid is decomposed, and dissolve out the resulting sodic sulphocyanate with hot alcohol or water. Ferricyanide of potassium heated with hydrated sodic hyposulphite is first converted, with separation of sulphur and evolution of sulphurous anhydride, into ferrocyanide, which is then converted, as above, into sulphocyanate and sulphide of sodium. (A. Fröhde, Pogg. Ann. cxix. 317.)

Sulphocyanate of sodium crystallises in rhombic tables, very deliquescent, and very soluble in alcohol.

SULPHOCYANATE OF STRONTIUM, $\mathrm{Sr''Cy^2S^2.3H^2O}$, forms deliquescent nodules, very soluble in water and in alcohol.

SULPHOCYANATE OF THALLIUM, TlCyS, is obtained. by mixing the solution of the carbonate with sulphocyanate of potassium, in small shining needles (Kuhlmann. Compt. rend. xv. 607). The crystals are quadratic, having however a monoclinic aspect, in consequence of irregular development. Observed combinations, $\infty P \,.\, P\infty$; and $\infty P\infty \,.\, \infty P \,.\, P\infty$. Angle $\infty P : P\infty = 128°\ 20{\cdot}3'$; $\infty P : P\infty = 116°\ 1'$; $P\infty : P\infty$, in the basal principal section[*] = 76° 40·6′. Twins with the combination-face $P\infty$. No distinct cleavage. (W. H. Miller, Proc. Roy. Soc. xiv. 555.)

SULPHOCYANATE OF TIN.—*Stannous hydrate* precipitated by ammonia, dissolves for the most part in sulphocyanic acid, leaving a light orange-coloured residue; the solution, when boiled, deposits stannous oxide, and leaves, on further evaporation, lemon-yellow *stannous sulphocyanate*, $Sn''Cy^2S^2$. This salt, when heated, becomes brown and black without change of form, and finally melts, leaving a black residue, which burns away with a glimmering violet-red light. It dissolves in water and in absolute alcohol, the aqueous solution appearing blue by reflected light. Potash separates black stannous oxide, and the evaporated solution yields tabular crystals of a double salt. Stannous sulphocyanate dissolves in sulphocyanate of potassium, with separation of brown stannous sulphide; and the filtrate first yields crystals of stannous sulphocyanate, then decomposes on further evaporation.—*Stannic hydrate* dissolves but very slightly in sulphocyanic acid. (L. Clasen, J. pr. Chem. xcvii. 349.)

SULPHOCYANATES OF URANIUM.—The *uranous salt* is dark-green, soluble, and crystalline.—The *uranic salt* is soluble in water, insoluble in alcohol.

SULPHOCYANATE OF ZINC, $Zn''Cy^2S^2$.—Deposited from alcohol in anhydrous crystals, very soluble in water. It dissolves also in ammonia, and the solution yields, by evaporation, rhomboïdal prisms of *sulphocyanate of zincammonium*, $(N^2H^6Zn'')''Cy^2S^2$, which are decomposed by water.

SULPHOCYANIC ANHYDRIDE, $C^2N^2S = Cy^2S$. *Cyanic Sulphide. Sulphide of Cyanogen.* (F. Linnemann, Ann. Ch. Pharm. cxx. 36.)—This compound is formed by the action of cyanic iodide on argentic sulphocyanate:

$$AgCyS + CyI = AgI + Cy^2S.$$

It is most easily prepared by mixing an ethereal solution of cyanic iodide with an equivalent quantity of argentic sulphocyanate, evaporating with constant stirring, and leaving the residual powder to itself for some hours in small closed vessels. The sulphocyanic anhydride may be separated from the argentic iodide by sublimation, or better, by extraction with boiling carbonic disulphide. The solution, if quickly filtered at the boiling heat, and then cooled to 0°, deposits the compound in crystals, which may be purified by drying in a vacuum over oil of vitriol.

Sulphocyanic anhydride is likewise produced by the action of sulphide of iodine, I^2S, on cyanide of silver; of sulphide of chlorine, Cl^2S, on cyanide of mercury; and of iodide of cyanogen on sulphide of silver. The product which Lassaigne obtained (in 1828) by treating cyanide of mercury with sulphide of chlorine, was nothing else than sulphocyanic anhydride. In preparing the compound by this process, a secondary product is likewise obtained, consisting of a white powder, insoluble in carbonic disulphide, but soluble in ether, and having, according to Linnemann's analyses, the composition $Cy^2S.HgCy$.

Sulphocyanic anhydride forms limpid rhombic tables or laminæ, which smell like iodide of cyanogen, and volatilise slowly on exposure to the air. It sublimes between 30° and 40°, melts at 60°, and solidifies in the crystalline form. When heated for some time in moist air, it decomposes. It dissolves in *ether*, *alcohol*, and *water*, and crystallises from solutions supersaturated while hot. It is easily decomposed by dilute *sulphuric acid*, also by *nitric* and by *hydrochloric acid*. With *iodide of potassium*, it gives off iodine; with aqueous *cyanide of potassium*, it evolves hydrocyanic acid; by fusion with *hydrate of potassium*, it yields ammonia, carbonic anhydride, sulphide, and sulphocyanate of potassium; with *potassium*, it forms cyanide and sulphocyanate of potassium; with *alcoholic potash-solution*, cyanate and sulphocyanate of potassium. With *nascent hydrogen*, *sulphydric acid*, and *monosulphide of potassium*, it decomposes as shown by the equations:

$$\begin{aligned} Cy^2S + H^2 &= HCy + HCyS \\ Cy^2S + H^2S &= HCy + HCyS + S \\ Cy^2S + K^2S &= KCy + KCyS + S. \end{aligned}$$

With *ammonia*, sulphocyanic anhydride forms the compound $(NH^3)^2Cy^2S = \left.\begin{matrix}NH^3Cy\\H\end{matrix}\right\}S$ (just as sulphydric acid, H^2S, forms $\left.\begin{matrix}NH^4\\H\end{matrix}\right\}S$), which separates as a crystalline powder on passing dry ammonia-gas into an ethereal solution of the anhydride. This compound dissolves easily in absolute alcohol; melts without decomposition at 94°; gives off ammonia with alkalis, and decomposes, in aqueous solution, into sulphocyanate of ammonium, and probably cyanamide.

The aqueous solution of sulphocyanic anhydride decomposes very quickly, depositing a yellow or orange-red powder, resembling persulphocyanogen (iv. 380), but of different composition, and perhaps consisting, for the most part, of a polymeric modification of sulphocyanic anhydride—namely, the anhydride of sulphocyanuric acid: this compound appears also to be the chief product of the decomposition of sulphocyanic anhydride in moist air. The acid solution remaining after the deposition of this powder, contains sulphocyanic acid (as chief product), hydrocyanic acid, sulphocyanate and sulphate of ammonium; it, moreover, gives off carbonic anhydride, and probably also carbonic oxide. (Linnemann.)

Iodocyanic Sulphide, CyIS.—This appears to be the composition of a red-brown, very volatile, and easily decomposible liquid, formed, together with iodide of silver, by treating sulphocyanate of silver with an ethereal solution of iodine. (Linnemann.)

SULPHOCYANIC ETHERS. Several sulphocyanates of monatomic alcohol-radicles are known, also the sulphocyanate of ethylene.

Allylic Sulphocyanate. *Volatile Oil of Mustard. Essence de Moutarde. Senföl.* $C^4H^5NS = C^3H^5.CyS = \left.\begin{matrix}Cy\\C^3H^5\end{matrix}\right\}S = \left.\begin{matrix}(CS)''\\C^3H^5\end{matrix}\right\}N$. (Boutron and Robiquet, J. Pharm. xvii. 296.—Henry and Plisson, *ibid.* xvii. 451.—Dumas and Pelouze, Ann. Ch. Phys. [2], liii. 181.—Aschoff, J. pr. Chem. iv. 314.—Robiquet and Bussy, Ann. Ch. Phys. [2], lxxxii. 328.—Boutron and Frémy, J. Pharm. xvi. 112.—Löwig and Weidmann, J. pr. Chem. xix. 218.—Will, Ann. Ch. Pharm. lii. 1.—Wertheim, *ibid.* lv. 297.—Gerhardt, Ann. Ch. Phys. [3], xiv. 125; *Traité*, ii. 409.—Gm. x. 41.)

This ether, or essential oil, is obtained from the seeds of black mustard by distillation with water, and exists, together with oil of garlic, in the oils produced in like manner from other cruciferous plants. It does not exist ready-formed in these plants, at least not in the dry parts, such as the seed. Its production requires the presence of water, and appears to depend upon the action of myrosin, a substance analogous to the emulsion of bitter almonds, or another substance, myronic acid, likewise existing in these plants in the form of a potassium-salt. [See MYRONIC ACID and MYROSIN, iii. 1073, 1075.] The seed of white mustard, which contains myrosin but not myronic acid, does not yield allylic sulphocyanate when distilled with water.

Allylic suphocyanate is formed artificially: 1. From myronic acid, by distilling myronate of barium or potassium with a caustic alkali (iii. 1070).—2. From allylic iodide, by the action of potassic or argentic sulphocyanate.—3. From allylic sulphide (i. 143), by treating the precipitate formed by the action of mercuric chloride on oil of garlic with potassic sulphocyanate (Wertheim). According to Hlasiwetz (Ann. Ch. Pharm. lxxi. 28), the precipitate formed by mixing the alcoholic solutions of oil of asafœtida and mercuric chloride, also yields allylic sulphocyanate when distilled with sulphocyanate of potassium.

Preparation.—*a.* From mustard-seed. The seed of black mustard is bruised and macerated for about twelve hours with 3 to 6 pts. of cold water, and then distilled, as long as any oil passes away with the water. The distillation is best conducted by passing steam into the still. A saturated solution of mustard-oil in water then passes over, and the excess of oil settles to the bottom. The aqueous solution, which contains a considerable quantity of the oil, may be advantageously used for macerating fresh portions of seed. 1000 pts. of mustard-seed macerated with fresh water yield from 2 to 7 pts. of oil; but if water saturated with the oil by repeated distillation be used, the product may amount to 10 or 11 parts.

The crude oil is mostly yellowish; it is purified by rectification, after drying over chloride of calcium. Pure sulphocyanate of allyl then passes over, between 145° and 150°.

b. From allylic iodide.—The iodide dissolved in alcohol is distilled with sulphocyanate of potassium; and the distillate mixed with water is rectified, the pure oil passing over, between 145° and 150° (Zinin, Ann. Ch. Pharm. xcv. 128). Or 1 at. iodide of allyl and 1 at. sulphocyanide of potassium are enclosed, together with a little water, in a sealed glass tube, and heated for some hours to 100°; water is then added, which dissolves the iodide of potassium and separates the allylic sulphocyanate; and the latter is rectified. (Berthelot and De Luca, Ann. Ch. Phys. [3], xliv. 495.)

Allylic sulphocyanate is obtained with still greater facility by the action of allylic iodide on sulphocyanate of silver. The action takes place at ordinary temperatures, iodide of silver being formed; while the iodide of allyl disappears, and is replaced by oil of mustard. At 100° sulphide of silver is formed. (Berthelot and De Luca.)

Properties.—Allylic sulphocyanate is a transparent colourless oil, of strong refracting power, and possessing in the highest degree the sharp penetrating odour of black mustard. The smallest quantity of the vapour excites tears, and is apt to produce inflammation of the eyes. It has a burning taste, and rapidly blisters the skin. Specific gravity = 1·015 at 20° (Dumas and Pelouze), 1·009 to 1·010 at 15° (Will). Boils at 148° (Will). Vapour-density, 3·54 (Will); calculated, 3·42. Refracting power = 1·516 (Will).

It is sparingly soluble in *water*, but dissolves very readily in *alcohol* and *ether*. It dissolves *sulphur* and *phosphorus* with tolerable facility when heated, these bodies separating in the crystalline form on cooling.

Decompositions.—1. Oil of mustard kneaded with alumina yields, by *dry distillation*, carbonic anhydride, carburetted hydrogen, and a small quantity of sulphydric acid, together with water. (Fontenelle.)

2. Exposed to daylight for three years in well-closed vessels, it gradually becomes brownish-yellow, and deposits an orange-yellow amorphous substance having the aspect of persulphocyanogen. This substance, when heated, swells up, assumes a dark colour, gives off a strong odour of mustard-oil, and leaves a dull but perfectly combustible charcoal. It dissolves in warm potash-solution, forming a yellow liquid, from which acetic acid precipitates light-yellow flocks; and the liquid filtered therefrom still gives a light-yellow precipitate with acetate of lead, but does not redden ferric salts, and therefore does not contain sulphocyanic acid. (Will.)

3. The aqueous solution of the oil, after exposure to the air for some hours, loses its sharpness, but retains its taste and mustard odour, and deposits a grey powder containing sulphur (Thibierge). The oil undergoes no change by exposure to the air or to oxygen, even for a considerable time, becoming neither acid nor alkaline. (Boutron and Robiquet.)

4. When *chlorine-gas* is very slowly passed into a retort filled with oil of mustard, very volatile crystals are formed, having a silky lustre (with evolution of hydrochloric acid, according to Dumas and Pelouze). These crystals become coloured and decompose when exposed to the air, and are dissolved by a large excess of chlorine, yielding a viscid, no longer crystallisable liquid. Potash-ley converts them into a resinous substance insoluble in potash. They are insoluble in water and in ether, but dissolve in alcohol in all proportions. (Boutron and Frémy.)

5. *Bromine* acts upon oil of mustard with frothing and evolution of heat, and forms a brown resin nearly insoluble in water; the solution contains sulphuric and hydrobromic acid. (Aschoff.)

6. *Iodine* dissolves quickly in the oil, forming a dark red-brown liquid. (Aschoff.)

7. When oil of mustard is treated with moderately strong *nitric acid*, a brisk reaction takes place, the oil becoming thick, assuming a green colour, and being converted into a resinous substance called nitrosinapylic resin. The mother-liquor contains oxalic acid and a nitro-acid called nitrosinapylic acid, of waxy consistence, soluble in water, insoluble in alcohol and ether. The solution gives yellow precipitates with lead- and silver-salts. The barium-salt is a yellow powder, soluble in water, and gives by analysis 18·23 per cent. carbon, 1·66 hydrogen, 39·25 baryta, 2·74 sulphur, and 21·96 oxygen, which, if the small quantity of sulphur be neglected, may be represented by the formula $C^{12}H^6Ba''(NO^2)^2N^2O^4$, making that of the acid $C^6H^4(NO^2)NO^2$.

8. When oil of mustard is completely oxidised by *nitric* or by *chromic acid*, large quantities of formic and acetic acids are produced, together with a small quantity of propionic acid.

9. *Aqueous potash*, *soda* and *baryta*, also the *oxides of lead*, *silver*, and *mercury*, in presence of water, convert oil of mustard into sinapoline (p. 311), with formation of a metallic sulphide and carbonate: *e.g.*,

$$\underset{\substack{\text{Oil of}\\\text{mustard.}}}{2C^4H^5NS} + 3Pb''O + H^2O = \underset{\text{Sinapoline.}}{C^7H^{12}N^2O} + 2Pb''S + Pb''CO^3.$$

For this decomposition the presence of water is absolutely necessary; the same oxides, in the dry state, abstract the sulphur but slowly and imperfectly from oil of mustard.

When oil of mustard is boiled for some time with strong *soda-ley*, in such a manner that the vapour may be condensed and flow back again, a large quantity of ammonia is evolved, and an oil of fishy odour is produced, which may be freed from the last traces of sulphur by means of potash and hydrate of lead; after washing with dilute acid and with water, and subsequent rectification, it is colourless, and exhibits the composition of allylic peroxide, C^3H^5O. It forms a crystalline compound with nitrate of silver. (Hlasiwetz, J. pr. Chem. li. 369.)

10. An *alcoholic solution of potash* or *soda* acts very differently from the aqueous solution. When oil of mustard is dropped into a concentrated alcoholic solution of potash, great heat is produced, which, if care be not taken to add the liquid slowly, may rise in a few seconds to violent ebullition, and occasion the projection of the contents of the vessel. No permanent gas is evolved, excepting perhaps a little ammonia.

The brown-red mixture exhibits, instead of the pungent odour of oil of mustard, merely a mild garlic odour; deposits, after a while, crystals of neutral potassic carbonate with 1 at. water; and when decanted from these crystals and mixed with water, is resolved, with milky turbidity, into aqueous sulphosinapic acid (p. 526), holding in solution a certain quantity of oil which may be dissolved out by ether, and an oil which sinks to the bottom; and if the mixture has been heated to the boiling-point, is dark-coloured, and contains insoluble flakes. (Will.)

The *peculiar oil* obtained by keeping the mixture cold, after being separated from the aqueous sulphuric acid by collecting it on a wet filter, purified from potash by washing with water, rectified with solution of common salt, and freed from the water, which makes it turbid, by standing for several days over chloride of calcium, and decantation, is transparent and colourless; has a density of 1·036 at 14°; a mild alliaceous odour; a taste which is not burning, but cooling; boils between 115° and 118°; but is partially decomposed by distillation, even in a stream of gas, ammonia being formed, as shown by the vapour browning turmeric-paper slightly, and a brown resin remaining, which gives off a large quantity of ammonia when more strongly heated, and from which, by continued boiling with water, a volatile alkaloïd, not yet further examined, may be extracted. The oil, when boiled with baryta-water, forms sulphide of barium, and a non-volatile substance, which remains in solution, and appears to be an alkaloïd. From lead-salts and silver-salts it also precipitates the sulphides on boiling. It forms a precipitate with alcoholic mercuric chloride, and, if the solution be not too dilute, likewise with alcoholic stannic chloride. It is sparingly soluble in water, but dissolves in all proportions in alcohol and ether. (Will.)

Its composition, as determined by analysis, is as follows :—

			The oil once,	*twice,*	*three times rectified.*
C^{14}	168	50·76	50·35	50·20	
N^{3}	42	12·69	12·30	10·40	9·73
H^{25}	25	7·55	7·88	7·84	
S^{2}	64	19·33	20·50		
O^{2}	32	9·67	8·97		
	331	100·00	100·00		

As the oil gives off ammonia after each rectification, whereby the amount of nitrogen is diminished in greater proportion than that of the other elements, it is probable that the original oil before the first rectification was $C^{14}H^{25}N^{3}S^{2}O^{2}.NH^{3} = C^{14}H^{28}N^{4}S^{2}O^{2}$ (or $C^{7}H^{14}N^{2}SO$), and therefore $= C^{7}H^{12}N^{2}O$ (sinapoline) + $H^{2}S$. (Will.)

According to this assumption, the equation for the decomposition of oil of mustard by alcoholic potash should be the following:

$$3C^{4}NH^{5}S + 3KHO + H^{2}O = K^{2}CO^{3} + C^{4}H^{6}NKS^{2} + C^{7}H^{14}N^{2}SO.$$

11. When oil of mustard is mixed with pulverised *soda-lime*, and heated for some time to 120° in a sealed tube, the sharp mustard odour is found, on opening the tube, to be replaced by an aromatic alliaceous odour; and on distilling the liquid, oxide of allyl (i. 142) is obtained, while sulphocyanate of sodium remains, often mixed with sulphide of sodium, produced by the secondary action of the excess of soda on the sulphocyanate (Wertheim):

$$2(C^{3}H^{5}.CNS) + Na^{2}O = (C^{3}H^{5})^{2}O + 2NaCNS.$$

12. From an alcoholic solution of the oil, metallic salts, e. g. *mercuric* and *platinic chloride*, also *silver-* and *lead-salts* (the latter at the boiling heat), separate metallic sulphides. (Will.)

Dry pulverised *hydrate of potassium* decomposes oil of mustard in a similar manner to the alcoholic solution of potash; but the products are less definite, because it is difficult to prevent too great a rise of temperature.

13. *Monosulphide of potassium* heated with oil of mustard in a sealed tube, to 100° or a little higher, forms sulphocyanate of potassium and oil of garlic:

$$2(C^{3}H^{5})CNS + K^{2}S = 2KCNS + (C^{3}H^{5})^{2}S.$$

If a polysulphide of potassium be heated in a similar manner with oil of mustard, and the product distilled, a solution is obtained which yields delicate crystalline needles, having a most intense odour of asafœtida.

14. *Potassium* decomposes dry oil of mustard completely, even at ordinary temperatures; on applying a gentle heat, sulphocyanate of potassium and sulphide of allyl are formed, together with a gas, which has not been examined.

Many of the *heavy metals* decompose oil of mustard, abstracting the sulphur. Mercury is quickly blackened when shaken up with the oil and water; and copper vessels in which mustard-oil is distilled, become coated with sulphide of copper.

Combinations—Allylic sulphocyanate unites with alkaline sulphides, forming compounds of the form $C^4H^5NS.M^2S$.—The *potassium-salt*, $C^4H^5NS.K^2S$, is deposited as a white granular powder, on mixing the alcoholic solutions of potassic monosulphide and allylic sulphocyanate, the former slightly in excess, and evaporating at a gentle heat.—Another salt, containing $2C^4H^5NS.K^2S$, separates from the mother-liquor of the preceding, when left over oil of vitriol, in needle-shaped crystals having a scarcely perceptible yellowish tinge.—The *barium-salt*, $C^4H^5NS.Ba''S$, is formed by gradually adding oil of mustard to a warm yellow solution of barium-sulphide, till its odour becomes permanent. The filtrate yields, on cooling, laminar efflorescent crystals containing 3 at. water. (Will.)

With alkaline sulphydrates it unites in like manner, forming salts of allylsulphocarbamic or sulphosinapic acid (*q.v.*); *e.g.*, $C^3H^5.CNS + KHS = \left.\begin{matrix}C^3H^5.H\\(CS)''\\K\end{matrix}\right\}\begin{matrix}N\\S\end{matrix}$.

Allylic sulphocyanate unites readily with *ammonia*, forming thiosinamine, $C^4H^5NS.NH^3$ = sulphocyanate of allylammonium, $\left.\begin{matrix}CN\\NH^3(C^3H^5)\end{matrix}\right\}S$, or allyl-sulphocarbamide, $\left.\begin{matrix}(CS)''\\C^3H^5\\H^3\end{matrix}\right\}\begin{matrix}N\\N\end{matrix}$. With the *alcoholic ammonia*, in like manner, it forms thiosinamines in which the typic hydrogen is more or less replaced by alcohol-radicles: thus with *ethylamine*, it forms ethylthiosinamine or ethyl-allylsulphocarbamide, $C^4H^5NS.NH^2(C^2H^5) = \left.\begin{matrix}(CS)''\\C^3H^5\\C^2H^5.H^2\end{matrix}\right\}\begin{matrix}N\\N\end{matrix}$ (see THIOSINAMINE); and with *triethylphosphine*, it forms triethyl-allyl-sulphocarbophosphamide, $C^4H^5NS.P(C^2H^5)^3 = \left.\begin{matrix}(CS)''\\C^3H^5\\(C^2H^5)^3\end{matrix}\right\}\begin{matrix}N\\P\end{matrix}$. See PHOSPHORUS-BASES (iv. 616).

Amylic Sulphocyanate, $C^6H^{11}NS = \left.\begin{matrix}CN\\C^5H^{11}\end{matrix}\right\}S = \left.\begin{matrix}(CS)''\\C^5H^{11}\end{matrix}\right\}N$. (Henry, Ann. Ch. Phys. [3] xxv. 248.—Medlock, Ann. Ch. Pharm. lxix. 214.)—Obtained by distilling, in a capacious retort, about equal volumes of crystallised amylsulphate and sulphocyanate of potassium. It is a colourless very mobile liquid, which after drying and rectification, boils constantly at 197°. Specific gravity = 0·905 at 20°. It has a pungent alliaceous odour, and burns with white smoky flame. It is but little attacked by sulphuric acid. By boiling with nitric acid, it is converted into amylsulphurous acid.

Ethylic Sulphocyanate, $C^3H^5NS = \left.\begin{matrix}CN\\C^2H^5\end{matrix}\right\}S = \left.\begin{matrix}CS''\\C^2H^5\end{matrix}\right\}N$. (Cahours, Ann. Ch. Phys. [3] xviii. 264.—Löwig, Pogg. Ann. lxvii. 101.—Muspratt, Ann. Ch. Pharm. lxv. 253.)—This ether is prepared:—1. By saturating a concentrated solution of potassic sulphocyanate with ethylic chloride. As soon as the reaction, which is slow, (but may be accelerated by sunshine) is complete, the liquid is to be diluted with an equal bulk of water and distilled, the distillate mixed with twice its volume of pure ether, and sufficient water added to separate the ethereal solution of ethylic sulphocyanate. The ether is then drawn off by distillation, and the remaining ethylic sulphocyanate is purified by rectification over chloride of calcium.—2. By distilling equal parts of calcic ethylsulphate and potassic sulphocyanate, both in concentrated solution.

Ethylic sulphocyanate is a mobile, colourless, strongly refracting liquid, having a taste of anise, and a pungent odour like that of mercaptan. Boils at 146°. Specific gravity of liquid = 1·020 at 16°; of vapour = 3·018. It is insoluble in *water*, but *alcohol* and *ether* dissolve it in all proportions.

Ethylic sulphocyanate is rapidly decomposed by *nitric acid*, yielding ethylsulphurous acid, with only a small quantity of sulphuric acid. The same acid is formed on treating the ether with *hydrochloric acid* and *chlorate of potassium*, the reaction being often so violent as to set the volatile products on fire.

Chlorine gradually attacks ethylic sulphocyanate, forming chloride of cyanogen, and a heavy oil soluble in water.—*Bromine* attacks it violently, forming crystallisable products.

When heated to 100° in a sealed tube with *aqueous potash*, it is converted into ethylic disulphide, with formation of potassic cyanide and cyanate (Brüning, Ann. Ch. Pharm. civ. 193):

$$2C^2H^5CyS + 2KHO = (C^2H^5)^2S^2 + KCy + KCyO + H^2O.$$

On boiling [the ether with *alcoholic potash*, ammonia is given off, together with ethylic disulphide. With an alcoholic solution of potassic monosulphide, it forms sulphide of ethyl and sulphocyanate of potassium, without evolution of ammonia.

The alcoholic solution of ethylic sulphocyanate does not precipitate metallic solutions.

Dry *ammonia-gas* forms, with ethylic sulphocyanate, a small quantity of a body having the composition of ethyl-sulphocarbamide, $(CS)''(C^2H^5)H^3N^2$.—With aqueous ammonia of ordinary strength, black uncrystallisable products are formed; with excess of dilute aqueous ammonia, the products formed are cyanide of ammonium, carbamide, and disulphide of ethyl:

$$2(C^2H^5.CNS) + 2NH^3 + H^2O = (NH^4)CN + CN^2H^4O + (C^2H^5)^2S^2.$$

Ethylamine likewise decomposes ethylic sulphocyanate. (Jeanjean, Compt. rend. lv. 330; see also Kremer, J. pr. Chem. lxxiii. 365; Jahresb. 1858, p. 401.)

With *triethylphosphine* at 100°, it forms a large quantity of triethylphosphine-sulphide, together with cyanide of triethylphosphonium (Hofmann, iv. 611):

$$C^2H^5.CNS + 2(C^2H^5)^3P = (C^2H^5)^3PS + (C^2H^5)^4P.CN.$$

Ethylenic Sulphocyanate, $C^4H^4N^2S^2 = \left.\begin{matrix}(CN)^2\\(C^2H^4)''\end{matrix}\right\}S^2 = \left.\begin{matrix}(\overset{''}{C}S)^2\\(C^2H^4)''\end{matrix}\right\}N^2.$ (Sonnenschein, J. pr. Chem. lxv. 257.—Buff, Ann. Ch. Pharm. xcvi. 302, c. 219; Jahresb. 1855, p. 610; 1856, p. 597.)—Produced by heating an alcoholic solution of ethylenic chloride (Dutch liquid), with an equivalent quantity of potassic sulphocyanate, to 100° in a sealed tube. Chloride of potassium then separates out, and on distilling off the volatile products from the filtered liquid, removing the remaining chloride and sulphocyanate of potassium with a little cold water, and dissolving the residue in hot water, a solution is obtained which yields crystals of ethylenic sulphocyanate on cooling.

Ethylenic sulphocyanate is moderately soluble in boiling water, and separates therefrom in stellate groups of small needles; easily soluble in warm alcohol, whence it crystallises in large, white, shining, rhombic plates. It melts at 90°, and solidifies at 83°; decomposes at a stronger heat, giving off a pungent odour, like that of burnt onions. With vapour of water it appears to distil undecomposed, the vapour attacking the eyes strongly, and exciting violent sneezing; it has a sharp burning taste. It dissolves in very dilute *nitric acid*, crystallises again in needles on cooling; but stronger nitric acid converts it into a crystalline acid, which, according to Buff, is identical with disulphetholic or ethylene-sulphurous acid, $C^2H^6S^2O^6$.

Acids do not separate sulphocyanic acid from ethylenic sulphocyanate. The alcoholic solution does not give the reaction of sulphocyanic acid with ferric salts till it has been boiled with potash. When boiled with *baryta-water*, it yields carbonate and sulphocyanate of barium. On boiling it with *plumbic hydrate*, sulphide of lead is formed, especially on addition of potash, and the solution gives, with ferric salts, the reaction of sulphocyanic acid. The alcoholic solutions of ethylenic sulphocyanate and *mercuric chloride* yield, after a while, a white precipitate (Sonnenschein). With *ammonia* it forms an easily soluble substance, which readily gives up sulphur to mercuric oxide (Buff).—With *triethylphosphine* it acts similarly to ethylic sulphocyanate, yielding sulphide of triethylphosphine and cyanide of ethylene-hexethyl-diphosphonium (Hofmann):

$$C^2H^4.C^2N^2S^2 + 4(C^2H^5)^3P = 2(C^2H^5)^3PS + (C^2H^4)''(C^2H^5)^6P^2.C^2N^2.$$

Hexylic Sulphocyanate, $C^6H^{13}.CNS$. (Pelouze and Cahours, Ann. Ch. Phys. [4] i. 5.)—Produced by heating hexylic chloride to 100° for several hours with alcoholic sulphocyanate of potassium. It is a nearly colourless fetid liquid, of specific gravity 0·922 at 12°, boiling at 215°—220°.

Methylic Sulphocyanate, $CH^3.CNS = \left.\begin{matrix}(CS)''\\CH^3\end{matrix}\right\}N.$ (Cahours, Ann. Ch. Phys. [3] xviii. 261.)—Obtained by distilling a concentrated solution of equal parts of potassic sulphocyanate and calcic methylsulphate. It is a colourless very mobile liquid, having an alliaceous and intoxicating odour. Boils between 132° and 133°. Specific gravity of liquid, 1·115 at 16°; of vapour = 2·570—2·549. It dissolves slightly in *water*; in all proportions in *alcohol* and *ether*. Chlorine attacks it very slowly in diffused light, producing fine crystals of chloride of cyanogen, together with a heavy yellow oil, which solidifies in contact with ammonia.—*Nitric acid* of ordinary strength dissolves it when warm, and deposits it again on cooling. By continued boiling with nitric acid, it is converted into methylsulphurous acid. It is scarcely attacked by *potash* at ordinary temperatures; but alcoholic potash decomposes it when heated, ammonia and methylic disulphide being given off, while cyanide and carbonate of potassium are found in the residue. With alcoholic *sulphide of potassium*, it forms sulphocyanate of potassium and sulphide of methyl.—Aqueous *ammonia* decomposes it quickly, forming a brown substance resembling ulmin, and a small quantity of a [illegible] body.

Naphthylic Sulphocyanate, $C^{10}H^7.CNS = \left.\begin{matrix}(CS)''\\ C^{10}H^7\end{matrix}\right\}N.$ (V. Hall, Phil. Mag. [4] xvii. 304.)—This ether is produced, together with naphthylamine, by distilling dinaphthyl-sulphocarbamide (obtained by digesting crude naphthylamine with carbonic disulphide) with phosphoric anhydride:

$$\left.\begin{matrix}(CS)''\\ (C^{10}H^7)^2\\ H^2\end{matrix}\right\}N^2 = \left.\begin{matrix}C^{10}H^7\\ H^2\end{matrix}\right\}N + \left.\begin{matrix}(CS)''\\ C^{10}H^7\end{matrix}\right\}N.$$

It is a crystalline compound, having a peculiar odour, easily fusible, insoluble in water, but very soluble in alcohol and ether. With *naphthylamine*, in alcoholic solution, it reproduces naphthyl-sulphocarbamide. With *aniline*, it yields phenyl-naphthyl-sulphocarbamide, $[(CS)''.C^6H^5.C^{10}H^7.H^2]N^2$.

Phenylic Sulphocyanate, $C^6H^5.CNS = \left.\begin{matrix}(CS)''\\ C^6H^5\end{matrix}\right\}N.$ (Hofmann, Proc. Roy. Soc. ix. 274, 487; Chem. Soc. Qu. J. xiii. 309.)—Produced by distilling phenyl-sulphocarbamide, $(CS)''.C^6H^5.H^3.N^2$, with phosphoric anhydride. After rectification over the latter, it is a colourless transparent liquid, smelling like oil of mustard, having a specific gravity of 1·135 at 15°, and boiling at 220°, under a pressure of 0·762 met. It distils unaltered with water, and even with hydrochloric acid, but is very easily decomposed by alkalis. *Alcoholic potash* converts it first into diphenyl-sulphocarbamide, then into diphenyl-carbamide. With *ammonia*, it yields phenyl-sulphocarbamide:

$$C^6H^5.CS.N + NH^3 = (CS)''.C^6H^5.H^3.N^2.$$

With amines, it unites in a similar manner: with *aniline*, for example, it forms diphenyl-sulphocarbamide, and with *naphthylamine*, phenyl-naphthylsulphocarbamide, isomeric or identical with that above described.

With *triethylphosphine* it unites so energetically that the mixture often takes fire: when, however, the action is duly regulated, triethyl-phenyl-sulphocarbophosphamide, $C^{13}H^{20}NPS = (CS)''(C^2H^5)^3.C^6H^5.N.P$, is produced (iv. 616). With *trimethylphosphine*, in like manner, it forms the compound $C^{10}H^{14}NPS = (CS)''(CH^3)^3(C^6H^5).NP$, which is an oily liquid, insoluble in water, slightly soluble in ether, easily in alcohol, and forming with hydrochloric acid the crystalline salt $C^{10}H^{14}NPS.HCl$.

SULPHOCYMENIC ACID. Syn. with THYMYLSULPHUROUS ACID. (See SULPHUROUS ETHERS.)

SULPHODRACONIC ACID. A conjugated acid, produced, according to Laurent, by treating oil of anise or tarragon with a large excess of sulphuric acid.

SULPHOFLAVIC ACID. See INDIGOSULPHURIC ACIDS (iii. 262).

SULPHOFORM. An oily liquid, produced in small quantity by distilling iodoform with mercuric sulphide (Bouchardat, J. Pharm. xxiii. 12). According to Eggert, however (Chem. Centr. 1857, p. 513), this product thus obtained is nothing but carbonic disulphide.

SULPHOFULVIC ACID. See INDIGOSULPHURIC ACIDS (iii. 262).

SULPHOGLUCIC ACID. Syn. with GLUCOSOSULPHURIC ACID (ii. 872).

SULPHOGLUTINIC ACID. The name applied by Berzolius to a glutinous acid, formed, together with other products, by the action of sulphuric anhydride in excess on naphthalene. (*Gerhardt's Traité*, iii. 468.)

SULPHOGLYCERIC ACID. $C^3H^8SO^6$. Syn. with GLYCEROSULPHURIC ACID (ii. 892).

SULPHOGLYCOLLIC ACID. $C^2H^4SO^5$. Syn. with ETHYLENE-SULPHURIC ACID. (See SULPHURIC ETHERS.)

SULPHOHIPPURIC ACID. $C^9H^9NSO^6 = C^9H^9NO^3.SO^3 = \left.\begin{matrix}C^7H^5O\\ (C^2H^2O)''\\ (SO^2)''\\ H^2\end{matrix}\right\}\begin{matrix}N\\ O^2.\end{matrix}$ (Schwanert, Ann. Ch. Pharm. cxii. 59; Jahresb. 1859, p. 328.)—Formed by treating hippuric acid with sulphuric anhydride. By converting the product into a lead-salt, decomposing with sulphydric acid, &c., it is obtained as a brown, amorphous, deliquescent mass, which is decomposed by nitrous acid, yielding sulphobenzoic acid, together with an oily liquid, probably glycollic acid.

The acid is dibasic. Its neutral *barium-salt* has the composition $C^9H^7Ba''NSO^6$. By boiling the acid with *plumbic hydrate*, a salt is obtained having approximately the composition $C^9H^7Pb''NSO^6$.

SULPHO-HYDROQUINONIC ACIDS. See HYDROQUINONE (iii. 217).

SULPHOMARGARIC ACID and **SULPHOLEIC ACID.** Oily acids, produced, according to Frémy (Ann. Ch. Phys. [2] lxv. 113), together with sulphoglyceric acid, by the action of strong sulphuric acid upon olein at low temperatures. The sulpholeic acid, being insoluble in the acid liquid, separates in the form of an oil from the sulphoglyceric acid, which remains dissolved. These two acids have not been separated, and consequently their composition has not been determined. They are both soluble in water and in alcohol, so likewise are their potassium-, sodium-, and ammonium-salts; the other salts are insoluble in water, slightly soluble in alcohol.

Sulpholeic acid is decomposed by water, yielding hydroleic and meta-oleic acids (iv. 195). Sulphomargaric acid yields similar products.

SULPHOLIGNIC ACID. A syrupy acid obtained by treating cotton, linen, sawdust, and other forms of cellulose, with strong sulphuric acid. It forms soluble salts with baryta and oxide of lead. (Gerhardt, ii. 548.)

SULPHOMANNITIC ACID. $C^6H^{14}O^6.3SO^3$.—An acid produced by dissolving mannite in strong sulphuric acid. It appears to be tribasic, forms gummy deliquescent salts with the alkalis and with oxide of lead, and a crystalline salt with baryta.

SULPHOMELANURENIC ACID. $C^3N^4H^4S^2 = CyH^2N.2CyHS = \left.\begin{matrix}Cy^3\\H^4\end{matrix}\right\}\begin{matrix}N\\S^2\end{matrix}$. *Sulphomellonic acid. Sulphydromellonic acid. Hydrothiomellone.* (Jamieson, Ann. Ch. Pharm. lix. 339.)—An acid obtained as a potassium-salt by boiling persulphocyanogen with sulphydrate of potassium:

$$\begin{aligned}2C^2N^2HS^3 + 3KHS + 2H^2O = C^3N^4H^3KS^2 &+ 2CNKS + CO^2\\ &+ 3H^2S \;\; + S^2.\end{aligned}$$

The resulting liquid neutralised with acetic acid yields a copious white precipitate, consisting of sulphur and sulphomelanurenic acid, which is to be washed and treated with cold aqueous ammonia, to dissolve out the acid and leave the sulphur; and the filtered solution, after being left to evaporate in a warm place, is to be boiled with animal charcoal, till it yields a perfectly white precipitate with acids.

Sulphomelanurenic acid is nearly insoluble in cold water, alcohol, and ether, slightly soluble in boiling water, which deposits it in very small needles. It is tasteless, but reddens litmus. It begins to decompose between 140° and 150°, and is resolved at a higher temperature into mellone and sulphydric acid:

$$\underset{\text{Sulphomelanurenic acid.}}{CyH^2N.2CyHS} = \underset{\text{Mellone.}}{NCy^3} + 2H^2S.$$

When heated with hydrochloric, sulphuric, or nitric acid, it is resolved into ammonia, sulphydric acid, and cyanuric acid:

$$CyH^2N.2CyHS + 3H^2O = NH^3 + 2H^2S + Cy^3H^3O^3.$$

Sulphomelanurenic acid is monobasic. Its potassium-salt, $2C^3N^4H^3KS^2.3H^2O$, forms shining colourless prisms, very soluble in water and in alcohol.—The *sodium-salt*, $2C^3N^4H^3NaS^2.3H^2O$, crystallises in large translucent plates having a fatty aspect, or in small scales resembling cholesterin.—The *barium-salt*, $C^6N^8H^6Ba''S^4.5H^2O$, forms colourless needles, having a fine adamantine lustre, and very soluble in water.—The *strontium-salt*, $C^6N^8H^6Sr''S^4.4H^2O$, forms large plates having a waxy lustre.—The *calcium-salt*, $C^6N^8H^6Ca''S^4.2H^2O$, forms shining crystals.—The *magnesium-salt*, $C^6N^8H^6Mg''S^4.6H^2O$, crystallises in small shining needles, very soluble in water.—The *silver-salt*, $C^3N^4H^3AgS^2$, is precipitated in white flocks, quite insoluble in water, on adding nitrate of silver to an ammoniacal solution of the acid. It blackens on exposure to light, but bears a temperature of 100° without decomposition.

SULPHOMELLONIC ACID. Syn. with SULPHOMELANURENIC ACID.

SULPHOMETHYLIC ACID. Syn. with METHYLSULPHURIC ACID. (See SULPHURIC ETHERS.)

SULPHOMOLYBDATES. See MOLYBDENUM, SULPHIDES OF (iii. 1043).

SULPHOMORPHIDE. A product of the action of sulphuric acid on morphine (iii. 1055).

SULPHONAPHTHALENE. $C^{10}H^{14}SO^2 = \left.\begin{matrix}C^{10}H^7\\C^{10}H^7\end{matrix}\right\}SO^2$. (Berzelius, Ann. Ch. Phys. [2] lxv. 290.—Laurent, Rev. Scient. viii. 587.)—This compound, which may be regarded as a double molecule of naphthalene, ($C^{10}H^8$), having two of its hydrogen-atoms replaced by sulphuryl, is formed by directing the vapour of sulphuric anhydride on an excess of fused naphthalene. A red syrupy liquid is thereby formed, from which the sulphonaphthalene may be separated by treating it with boiling water, and c [illegible] residue from aqueous alcohol.

Sulphonaphthalene crystallises from alcoholic solution in tasteless inodorous nodules. It melts at 70°, and solidifies on cooling to a transparent mass, which becomes electric by friction. At a higher temperature, it decomposes, giving off sulphurous anhydride. It is slightly soluble in water, more soluble in boiling alcohol, not attacked by boiling potash-ley. Nitromuriatic acid dissolves it at the boiling heat, without formation of sulphuric acid.

SULPHONAPHTHALIC ACID. $C^{10}H^8SO^3$. Syn. with NAPHTHYLSULPHUROUS ACID. (See SULPHUROUS ETHERS.)

Disulphonaphthalic Acid, $C^{10}H^8S^2O^6$. Syn. with NAPHTHYLENE-SULPHUROUS ACID. (See SULPHUROUS ETHERS.)

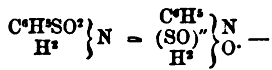
SULPHONAPHTHALIDAMIC ACID. Syn. with NAPHTHIONIC ACID (iv. 17).

SULPHONAPHTHANIC ACID. Syn. with SULPHONAPHTHALIC ACID.

SULPHONARCOTIDE. A product of the decomposition of sulphate of narcotine (iv. 28).

SULPHOPHENIC ACID. $C^6H^5.H.SO^4$. Syn. with PHENYLSULPHURIC ACID. (See SULPHURIC ETHERS.)

SULPHOPHENYLAMIDE. $C^6H^7NSO^2$ =



$\left.\begin{matrix}C^6H^5SO^2\\H^2\end{matrix}\right\}N = \left.\begin{matrix}C^6H^5\\(SO)''\\H^2\end{matrix}\right\}\begin{matrix}N\\O.\end{matrix}$ — *Sulphobenzolamide. Azoture phenylsulfureux. Azoture de sulfophenyle et d'hydrogène.* (Gerhardt and Chancel, Compt. rend. xxxv. 690.—Gerhardt and Chiozza, *ibid.* xxxv. 86; *Gerhardt's Traité*, iii. 74.)—Produced by the action of ammonia on sulphophenylic chloride. A convenient mode of preparing it is to pour the chloride on a large excess of pulverised ammonium-carbonate; the reaction commences immediately, and may be completed by gently heating the mortar in which the mixture is made, till the odour of the chloride is no longer perceptible. The product is then washed with cold water, which dissolves out the sal-ammoniac and the excess of ammonium-carbonate, and the residual sulphophenylamide is crystallised from a small quantity of boiling alcohol. It is also produced (together with sulphurous anhydride, ammonia, benzol, and a small quantity of phenylic sulphide) by heating phenylsulphite (sulphobenzolate) of ammonium. (Stenhouse, Proc. Roy. Soc. xiv. 351.)

Sulphophenylamide crystallises from alcohol in splendid nacreous scales (Gerhardt); from alcohol or water in laminæ resembling naphthalene, and melting at 153° (Stenhouse); according to Gerhardt, it is insoluble in water, very soluble in alcohol, soluble in boiling aqueous ammonia.

Sulphophenylamide contains two atoms of typic hydrogen, one or both of which may be replaced by metals or organic radicles. The following compounds have thus been obtained:—

Argentosulphophenylamide	$C^6H^6AgNSO^2$.
Benzosulphophenylamide	$C^6H^6(C^7H^5O)NSO^2$.
Argento-benzosulphophenylamide	$C^6H^5Ag(C^7H^5O)NSO^2$.
Dibenzosulphophenylamide	$C^6H^5(C^7H^5O)^2NSO^2$.
Benzacetosulphophenylamide	$C^6H^5(C^7H^5O)(C^2H^3O)NSO^2$.
Cumosulphophenylamide	$C^6H^5(C^{10}H^{11}O)NSO^2$.
Cumo-benzosulphophenylamide	$C^6H^5(C^{10}H^{11}O)(C^7H^5O)NSO^2$.
Phenylsulphophenylamide	$C^6H^6(C^6H^5)NSO^2$.
Succinosulphophenylamide	$C^6H^5(C^4H^4O^2)''NSO^2$.

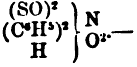
Argentosulphophenylamide, $C^6H^6AgNSO^2$, is obtained as a white crystalline precipitate on adding nitrate of silver to an alcoholic and ammoniacal solution of sulphophenylamide.

Succinosulphophenylamide, $C^{12}H^9NSO^2$, is formed by the action of succinic chloride on sulphophenylamide. The product, which is viscous at first, solidifies when treated with alcohol, and crystallises therefrom in very fine needles.

Phenylsulphophenylamide, or *Sulphophenylanilide*, $C^{12}H^{11}NSO^2$, is formed by the action of aniline on sulphophenylic chloride. The product remains viscous for a long time; but when dissolved in alcohol, it yields splendid prisms, with pyramidal faces, like small crystals of amethyst, which they also resemble in colour. They dissolve easily in alcohol and ether. (Chiozza and Biffi; *Gerhardt's Traité*, iii. 981.)

The other compounds in the preceding list have been already described under BENZAMIDE (i. 539, 540), and CUMINAMIDE (ii. 177).

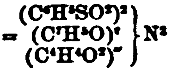
Disulphophenylamide, $C^{12}H^{11}NS^2O^4$ = $N.H.(C^6H^5SO^2)^2$ =



$\left.\begin{matrix}(\overset{''}{SO})^2\\(C^6H^5)^2\\H\end{matrix}\right\}\begin{matrix}N\\O^2.\end{matrix}$—

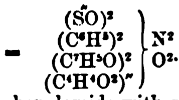
Produced by gently heating argentosulphophenylamide with sulphophenylic chloride; purified by crystallisation from ether.

Succino-dibenzo-disulphophenyldiamide, $C^{30}H^{24}N^2S^2O^8$ =



$$\left.\begin{matrix}(C^6H^5SO^2)^2\\(C^7H^5O)^2\\(C^4H^4O^2)''\end{matrix}\right\}N^2$$

=



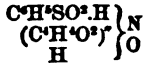
$$\left.\begin{matrix}(\overset{''}{S}O)^2\\(C^6H^5)^2\\(C^7H^5O)^2\\(C^4H^4O^2)''\end{matrix}\right\}\begin{matrix}N^2\\O^2\end{matrix}$$

.—This compound, obtained by heating argento-benzosulphophenylamide with succinic chloride, crystallises from ether in small needles.

SULPHOPHENYLIC or **PHENYLSULPHUROUS CHLORIDE.** $C^6H^5SO^2Cl$. (See SULPHUROUS ETHERS.)

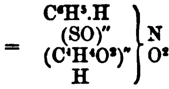
SULPHOPHENYLIC or **PHENYLSULPHUROUS HYDRIDE.** $C^6H^6SO^2$. —A compound formed by the action of reducing agents on the corresponding chloride. (See SULPHUROUS ETHERS.)

SULPHOPHENYLSUCCINAMIC ACID. $C^{10}H^{11}NSO^5$ =



$$\left.\begin{matrix}C^6H^5SO^2.H\\(C^4H^4O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$$

=



$$\left.\begin{matrix}C^6H^5.H\\(SO)''\\(C^4H^4O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$$

. (Gerhardt and Chiozza, Ann. Ch. Phys. [3] xlvii. 129.)—The ammonium-salt of this acid is obtained by evaporating an ammoniacal solution of succinosulphophenylamide, first at a gentle heat, then in a vacuum. A very thick syrup then remains, which alternately crystallises in concentric groups of silky fibres. This salt is very soluble in water and in alcohol, melts at 160°, giving off a large quantity of ammonia, and leaving an oil which, when dissolved in ammonia, yields crystals of sulphophenylamide. The aqueous solution of the ammonium-salt, mixed with a few drops of hydrochloric acid, deposits splendid needles, which melt between 155° and 160°, and have the composition of the original salt. The *silver-salt*, $C^{10}H^{10}AgNSO^5$, is deposited in beautiful needles on adding nitrate of silver to a solution of the ammonium-salt.

SULPHOPHLORAMIC ACID. An acid produced by heating phloramine (iv. 488) with strong sulphuric acid. On saturating the solution with carbonate of barium, decomposing the hot filtrate with sulphuric acid, and decolorising with animal charcoal, the acid is obtained in colourless needles. Its solution, even when very dilute, forms a deep violet colour with ferric chloride, like that produced by tyrosinsulphuric acid. (Hlasiwetz, Ann. Ch. Pharm. cxix. 199.)

SULPHOPHLORETIC ACID. $C^9H^{10}SO^6$.—This acid, produced by the action of sulphuric anhydride on phloretic acid, forms a very sour syrup, easily soluble in water and in alcohol. The *barium-salt*, $C^9H^8Ba''SO^6.3H^2O$, crystallises in hard apparently rhomboïdal crystals; it is insoluble in alcohol and ether, and gives off its water at 16°. The *calcium-salt*, $C^9H^8Ca''SO^6.4H^2O$, is crystalline; the *magnesium-salt*, $C^9H^8Mg''SO^6.5H^2O$, gummy. The *sodium-salt*, $C^9H^8Na^2SO^6.xH^2O$, forms hard, easily soluble, crystalline crusts, which give off their water at 260°. (Nachbaur, J. pr. Chem. lxxv. 45.)

SULPHOPHOSPHATES and **SULPHOPHOSPHITES.** See PHOSPHORUS, SULPHIDES OF (iv. 603, 604).

SULPHOPIANIC ACID. See OPIANIC ACID (iv. 206).

SULPHOPURPURIC ACID. See INDIGOSULPHURIC ACIDS (iii. 262).

SULPHOPYROMUCIC ACID. $C^5H^4SO^6$. By treating well-dried pyromucic acid with sulphuric anhydride, a yellow-brown syrup is obtained, which, by dilution, neutralisation with baryta, and evaporation, yields an indistinctly crystalline barium-salt, containing (at 150°) $C^5H^2Ba''SO^6$. (Schwanert, Ann. Ch. Pharm. cxvi. 268.)

SULPHOQUINIC ACID. Syn. with QUININE-SULPHURIC ACID (p. 26).

SULPHORETINYLIC ACID. An acid isomeric with sulphocumolic acid, obtained, according to Cahours and Gerhardt, by treating retinyl (iv. 98) with fuming sulphuric acid. Its barium-salt is less soluble than the sulphocumolate, and separates on evaporation in crystalline crusts, which have not the nacreous aspect of the sulphocumolate. (Gerhardt, iii. 388.)

SULPHORUFIC ACID. See INDIGOSULPHURIC ACIDS (iii. 262).

SULPHOSACCHARIC or **SULPHOGLUCIC ACID.** $C^{21}H^{18}SO^{27}$ =

$4C^6H^{12}O^6.SO^3$? (Peligot, Ann. Ch. Phys. [2] lxvii. 68.)—Prepared by treating glucose with 1½ pt. of strong sulphuric acid, mixing the materials by small quantities and in a cooled vessel. By saturating with carbonate of barium, and treating the filtrate with basic acetate of lead, a lead-salt is precipitated, containing (at 170°) 18·05 per cent. C, 2·5 H, 55·15 PbO, and 4·5 SO^3, agreeing approximately with the formula $C^{24}H^{40}Pb^4SO^{27}$.—By decomposing this lead-salt with sulphydric acid, sulphosaccharic acid is obtained in the form of a liquid, which reddens litmus, and has a sweet and sour taste, like that of lemonade. It does not precipitate barium-salts; in fact, nearly all its salts are soluble. It is very unstable, decomposes at ordinary temperatures in a vacuum, and quickly at the heat of the water-bath, into glucose and sulphuric acid.

SULPHOSALICYLIC ACID. $C^7H^6SO^6 = C^7H^6O^3.SO^3 = \left.\begin{array}{r}(C^7H^4O)''\\(SO)''\\H^2\end{array}\right\}O^4$.—This acid, discovered by Cahours (Ann. Ch. Phys. [3] xiii. 92), and more fully examined by Mendius (Ann. Ch. Pharm. ciii. 39; Jahresb. 1857, p. 319), is produced by exposing perfectly dry salicylic acid (prepared from wintergreen oil) to the vapour of sulphuric anhydride. The product dissolved in a small quantity of water is separated by filtration from unaltered salicylic acid; the filtrate is saturated with carbonate of barium; the resulting barium-salt, which separates partly as the filtrate cools, partly on evaporation, is decomposed by a slight excess of sulphuric acid; the filtered solution is partially saturated with carbonate of lead; the lead is precipitated by sulphydric acid; the concentrated filtrate is left over oil of vitriol till it deposits sulphosalicylic acid in crystals; and these are freed from the viscid mother-liquor by means of absolute alcohol.

Sulphosalicylic acid crystallises in long thin needles, which are dissolved in all proportions by *water*, *alcohol*, and *ether*, and absorb moisture from the air. It is a very strong and permanent acid. Its solution dissolves zinc with evolution of hydrogen, and is not decomposed by heating with nitric or hydrochloric acid, either dilute or concentrated; by boiling with a mixture of the two, however, it is resolved into sulphuric and salicylic acids, the latter being further converted into perchloroquinone (chloranil), which separates in yellow flocks. Sulphosalicylic acid melts at 120°, and decomposes at higher temperatures, giving off phenol and a sublimate of salicylic acid. (Mendius.)

Sulphosalicylates.—Sulphosalicylic acid is dibasic, forming neutral acid and double salts. They are all soluble in water (the lead and silver-salts, however, sparingly soluble), and nearly all are insoluble in alcohol and ether. With ferric salts, they produce a deep violet coloration, inclining more to red than that produced by salicylic acid. They do not give off the whole of their crystallisation-water below 180°—200°, and decompose at higher temperatures, with evolution of phenol; the acid salts also yield a sublimate of salicylic acid.

The *ammonium-salt* is difficult to obtain pure, its solution turning brown and giving off ammonia when evaporated.

Barium-salts.—The *neutral salt*, $C^7H^4Ba''SO^6.3H^2O$, prepared as above, is crystalline, easily soluble in hot, less easily in cold water.—The *acid salt*, $C^{14}H^{10}Ba''S^2O^{12}.4H^2O$, or $C^7H^4Ba''SO^6.C^7H^6SO^6.4H^2O$, crystallises in oblique, irregular, six-sided prisms.

The *calcium-salt*, $C^7H^4Ca''SO^6.H^2O$, forms hemispherical groups of silky needles.

Copper-salts.—The *neutral salt*, $C^7H^4Cu''SO^6$ (at 180°), obtained by decomposing the barium-salt with cupric sulphate, forms cauliflower-shaped masses of crystals, extremely soluble in water.—A *basic salt*, $C^7H^4Cu''SO^{10}.Cu''O.2H^2O$, is obtained as a green crystalline powder by digesting the acid with recently precipitated cupric oxide and evaporating.

The *lead-salt*, $C^7H^4Pb''SO^6$, crystallises indistinctly in small round nodules.

The *magnesium-salt*, $C^7H^4Mg''SO^6.3H^2O$, crystallises in long irregularly crossing rectangular prisms, which become opaque in the air, and dissolve very easily in water. The solution, mixed with sal-ammoniac and ammonia, is not precipitated by phosphate of sodium till boiled.

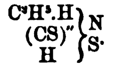
Potassium-salts.—The *neutral salt*, $C^7H^4K^2SO^6.2H^2O$, is permanent in the air, very soluble in water, less soluble in alcohol, and may be crystallised from the latter. —The *acid salt*, $C^7H^5KSO^6.2H^2O$, separates from a hot concentrated solution in spherical groups of needles.—Another *acid salt*, $C^7H^4K^2SO^6.C^7H^5KO^6.H^2O$, separates from a solution of the neutral salt mixed with a small quantity of free acid.—*Potassio-cupric* and *potassio-plumbic sulphosalicylates* have been obtained as uncrystallisable masses.

The *silver-salt*, $C^7H^4Ag^2SO^6.H^2O$, obtained by digesting recently precipitated silver-oxide in the hot aqueous acid, is sparingly soluble in cold, easily soluble in hot water.

Sodium-salts.—The *neutral salt*, $C^7H^4Na^2SO^6.3H^2O$, forms transparent, colourless, oblique, six-sided prisms, which do not give off all their water till heated to 200°; it dissolves easily in water.—A *sodio-potassic salt*, $C^7H^4KNaSO^6.4H^2O$, obtained by neutralising the acid potassium-salt with carbonate of sodium, crystallises in rectangular prisms having a silky lustre.

The *zinc-salt*, $C^7H^4Zn''SO^6.3H^2O$, resembles the magnesium-salt.

Ethylic Sulphosalicylate, $C^7H^4(C^2H^5)^2SO^6$, is formed by the action of ethylic iodide on argentic sulphosalicylate, and separates from alcoholic solution in soft, kneadable, silky crystals, which are perfectly neutral, melt at 56°, and distil unaltered with water. (Mendius.)



SULPHOSINAPIC or **ALLYL-SULPHOCARBAMIC ACID.** $C^4H^7NS^2$ $= C^3H^5CyS.H^2S = \left.\begin{matrix}C^3H^5.H\\(CS)''\\H\end{matrix}\right\}\begin{matrix}N\\S.\end{matrix}$ (Will, Ann. Ch. Pharm. lii. 30.)—This acid is not known in the free state. Its salts may be regarded as compounds of allylic sulphocyanate (oil of mustard), with metallic sulphydrates, and those which are soluble may be produced by the direct union of these constituents; also by the action of allylic sulphocyanate on the alkaline solutions of the corresponding hydrates. The insoluble salts are formed by precipitation.

The *ammonium-salt*, $C^4H^{10}N^2S^2 = (C^3H^5)CNS.(NH^4)HS$, formed as above by direct combination, solidifies to a magma of colourless laminæ; it is very unstable, decomposing spontaneously at ordinary temperatures.

The *potassium-salt*, $C^4H^6KNS^3 = (C^3H^5)CyS.KHS$, separates by slow evaporation from an alcoholic or even an aqueous solution of potassic sulphydrate, to which mustard-oil is added as long as its odour is destroyed, in large rhombic plates; by quicker evaporation in smaller crystals. It may also be prepared by slowly dropping oil of mustard into a concentrated solution of potash in absolute alcohol; decanting the solution after several hours from the crystallised potassic carbonate, diluting it with water, and evaporating the pale-yellow filtrate to a syrup: this, when set aside, deposits shining crystals of potassic sulphosinapate. The salt cannot, however, be obtained quite pure.

The crystals of potassic sulphosinapate are transparent and colourless so long as they remain in the liquid, but on exposure to the air they become opaque and yellow, lose their form, and become partly insoluble in water. The aqueous solution of the recently prepared salt may be heated without giving off the odour of mustard-oil; but on mixing the heated solution with nitrate of silver, sulphide of silver is precipitated, and the odour of mustard-oil becomes perceptible. The dried salt, when heated, gives off mustard-oil, and yields a brown liver of sulphur. When decomposed by sulphuric acid, it yields a large quantity of sulphydric acid, but no sulphur.

The *sodium-salt*, $C^4H^6NaNS^2.3H^2O$, is formed by direct combination, and separates in nacreous laminæ, which are unctuous to the touch, and when heated, first melt, and then give off a large quantity of mustard-oil; it cannot be kept without decomposing.

The *barium-salt*, $C^8H^{12}Ba''N^2S^4.4H^2O = 2C^3H^5CyS.Ba''H^2S^2.4H^2O$, is obtained: (1) by heating oil of mustard with a solution of barium-sulphydrate containing alcohol; (2) by passing sulphydric acid gas through aqueous alcohol containing hydrate of barium and oil of mustard in suspension; (3) it is deposited from the mother-liquor of the alcoholic solution of the compound of allylic sulphocyanate and sulphide of barium (p. 519). It forms crystalline laminæ resembling the sodium-salt and very soluble.

The *calcium-salt*, as obtained by the second method of preparing the barium-salt, forms a slightly yellow transparent jelly, which decomposes in drying.

The *lead-salt*, $C^8H^{12}Pb''N^2S^4$, is obtained by adding neutral acetate of lead to a very dilute solution of the potassium-salt acidulated with acetic acid, as a white precipitate, which decomposes partially, even during washing and drying in a vacuum over oil of vitriol, and quickly at 100°, yielding oil of mustard, sulphide of lead, and free sulphur.

When decomposed by sulphuric acid, it gives off abundance of sulphydric acid, without the slightest odour of mustard-oil.

The soluble sulphosinapates yield with *copper-salts* a green precipitate, and with *silver-salts* a white precipitate, both of which quickly blacken and decompose, even when immediately thrown on a filter and washed with cold water.

SULPHOSINAPISIN. The name given by Henry and Garot to sulphocyanate of sinapine. (See SINAPINE, p. 308.)

SULPHOSUCCINIC ACID. $C^4H^6SO^7 = C^4H^6O^4.SO^3 = \left.\begin{matrix}(C^4H^3O^2)''' \\ (SO)'' \\ H^3\end{matrix}\right\}O^4.$ (Fehling, Ann. Ch. Pharm. xxxviii. 285; xlix. 203.)—Produced by exposing succinic acid to the vapour of sulphuric anhydride in a vessel externally cooled, and heating the resulting viscous mass to 40° or 50° for several hours. The product is dissolved in water, the solution saturated with carbonate of lead, the lead-salt decomposed by sulphydric acid, and the filtered solution evaporated in a vacuum over oil of vitriol.

Sulphosuccinic acid thus obtained forms mammellated crystals, very soluble in water, alcohol, and ether; it has a very sour taste, and decomposes quickly when heated, leaving an abundant carbonaceous residue. The crystals absorb moisture from the air; their aqueous solution is partially decomposed by evaporation over the water-bath.

Sulphosuccinates.—The acid is tribasic, the neutral sulphosuccinates of monatomic metals having the composition $C^4H^3M^3SO^7$. The acid saturates bases completely, and even decomposes acetates.

The *neutral ammonium-salt*, $C^4H^3(NH^4)^3SO^7.H^2O$, is obtained by placing a strong solution of the acid, together with aqueous ammonia, under a bell-jar, in the form of a syrup, which ultimately becomes filled with needles having an acid reaction.

Potassium-salts.—The *neutral* or *tripotassic salt*, $2C^4H^3K^3SO^7.3H^2O$, is obtained by saturating the acid with potassic carbonate and evaporating in a vacuum, as a syrup containing a few deliquescent crystals; but on adding a small quantity of acid to the liquid, it quickly solidifies to a crystalline pulp. The salt is insoluble in absolute alcohol. It gives off a third of its water in a vacuum, the rest when heated.—The *dipotassic salt*, $C^4H^4K^2SO^7.2H^2O$, obtained by adding sulphosuccinic acid to the neutral salt, is very soluble in water, and has an acid reaction.

The *neutral sodium-salt*, obtained by decomposing the *barium-salt* with sulphate of sodium, is also very soluble in water.

The *neutral barium-salt*, $C^8H^6\overset{''}{Ba}{}^3S^2O^{14}$ (at 100°), is a white precipitate, obtained by precipitating the neutral potassium-salt with barium-chloride; it is very soluble in nitric or hydrochloric acid; dissolves also in sulphosuccinic acid, the solution, when left in a vacuum, depositing crystals which appear to consist of an acid salt.

An *acid calcium-salt*, $C^4H^4Ca''SO^7$ (at 100°), is obtained by dissolving calcic carbonate in sulphosuccinic acid and evaporating to dryness.

The *magnesium-salt* is uncrystallisable. The sulphosuccinates of *manganese*, *iron*, *cobalt*, *nickel*, and *copper* appear to be soluble, inasmuch as the potassium-salt does not precipitate the solutions of these metals.

The *neutral lead-salt*, $C^8H^6\overset{''}{Pb}{}^3S^2O^{14}.3H^2O$, is a white precipitate, obtained by adding acetate of lead to an alkaline sulphosuccinate. A *basic salt*, $C^8H^6\overset{''}{Pb}{}^3S^2O^{14}.Pb''O$ (at 100°), is formed by treating the neutral salt with ammonia.

The *silver-salt* is a white precipitate, which decomposes completely during washing, acquiring a deep-green colour.

SULPHOSULPHAMYLIC ACID. Syn. with AMYLSULPHUROUS ACID. (See SULPHUROUS ETHERS.)

SULPHOSTANNATES and **SULPHOSTANNITES.** See TIN, SULPHIDES OF.

SULPHOTELLURATES and **SUPHOTELLURITES.** See TELLURIUM, SULPHIDES OF.

SULPHOTHYMIC ACID. Syn. with THYMYLSULPHUROUS ACID. (See SULPHUROUS ETHERS.)

SULPHOTOLUOLAMIDE or **SULPHOBENZYLAMIDE.** $C^7H^9NSO^2$.—This compound, homologous with sulphophenylamide, and prepared by a similar process (p. 523), crystallises from hot water in needles or in laminæ. When heated with pentachloride of phosphorus, it is converted into a thick oil, which is decomposed by water, with reproduction of the amide; when distilled with the pentachloride, it gives off a liquid which partly dissolves in water, the solution also yielding crystals of sulphotoluolamide. (Fittig, Ann. Ch. Pharm. cvi. 277.)

SULPHOTOLUYLIC CHLORIDE. $C^7H^7SO^2Cl$. Syn. with BENZYLSULPHUROUS CHLORIDE. (See SULPHUROUS ETHERS.)

SULPHOTOLYLAMIC or **BENZYLSULPHAMIC ACID.** $C^7H^9NSO^3 = \left.\begin{matrix}C^7H^7.H \\ (SO^2)'' \\ H\end{matrix}\right\}\begin{matrix}N \\ O\end{matrix}$ (E. Sell, Ann. Ch. Pharm. cxxvi. 153; Chem. Soc. Qu. J. [2] i. 186.) —

Produced by carefully mixing 9 pts. fuming sulphuric acid with 5 pts. finely divided toluidine (benzylamine), and gently heating the syrupy mass till it gives off abundance of sulphurous anhydride. The solution is mixed with cold water, decolorised by boiling with animal charcoal, and evaporated till it assumes a reddish-yellow colour; the acid then separates in light-yellow needles, which may be purified by recrystallisation from water. The first mother-liquor yields rhomboïdal crystals, probably of benzyldisulphamic acid (p. 480).

The sulphotolylamates or benzylsulphamates are mostly very soluble in water; the barium-salt crystallises in groups of laminæ; the silver-salt, $C^7H^8AgNSO^3$, in white laminæ, which turn grey when exposed to light.

SULPHOTRIPHOSPHAMIDE. $N^3PH^6S = \left.\begin{matrix}(PS)'''\\ H^6\end{matrix}\right\}N^3$. (H. Schiff, Ann. Ch. Pharm. ci. 299.)—This compound appears to be formed by the action of ammonia-gas on phosphoric sulphochloride:

$$PSCl^3 + 3NH^3 = 3HCl + N^3PSH^6.$$

The white mass formed by the reaction is decomposed slowly by cold, immediately by warm water, with evolution of sulphydric acid. Alcohol extracts sal-ammoniac from it, and at the same time decomposes the other body contained in it, which is probably sulphotriphosphamide.

Triphenyl-sulphotriphosphamide, $\left.\begin{matrix}(PS)'''\\ (C^6H^5)^3\\ H^3\end{matrix}\right\}N^3$, appears to be contained, together with hydrochlorate of aniline, in the white mass produced by the action of phosphoric sulphochloride on aniline. (Schiff.)

SULPHOVANADATES and **SULPHOVANADITES.** See VANADIUM, SULPHIDES OF.

SULPHOVINIC ACID. Syn. with ETHYLSULPHURIC ACID. (See SULPHURIC ETHERS.)

SULPHOVIRIDIC ACID. See INDIGOSULPHURIC ACID (iii. 262).

SULPHOXALENIDE. } See CYANOGEN, SULPHYDRATES OF (ii. 285).
SULPHOXAMIDE. }

SULPHOXYBENZOIC ACID. $C^7H^6SO^6 = C^7H^6O^3.SO^3$. (Griess, Zeitschr. Ch. Pharm. 1864, p. 538.)—This acid, isomeric with sulphosalicylic acid, is produced by dissolving sulphato-diazobenzoic acid * in warm concentrated sulphuric acid:

$$C^7H^4N^2O^2.SH^2O^4 = C^7H^6O^3.SO^3 + N^2.$$

It crystallises out when the evolution of gas has ceased, and is obtained by recrystallisation from water, in white laminæ, soluble in alcohol. It is dibasic, like sulphosalicylic acid. The neutral barium-salt, $C^7H^4Ba''SO^6$, crystallises in sparingly soluble prisms. By strong nitric acid, it is resolved into sulphuric and tritro-oxybenzoic acids.

The name sulphoxybenzoic acid was formerly applied by Griess (Jahresb. 1861, p. 418) to the compound $C^7H^6SO^2$, produced by the action of sulphydric acid on the platinum-salt of chlorhydrato-diazobenzoic acid (iv. 294).

SULPHUR. *Atomic Weight*, 3; *Symbol*, S. *Vapour-density* = 32, referred to hydrogen, or 2·218, referred to air as unity.

Sulphur (*sal*, *πῦρ*), or brimstone (*brenne-stone*), has been known from the earliest times. It occurs native, either in the form of transparent amber-coloured crystals (*virgin sulphur*), or in opaque, lemon-yellow, crystalline masses (*volcanic sulphur*). It is found principally in Sicily, in beds of a blue clay formation, considered to be more recent than the chalk. The sulphur is imbedded in a matrix of rock-salt, gypsum, and celestine. Similar beds containing sulphur exist in other parts of Europe and in Mexico. It is also found occasionally in primitive rocks, granite, mica, &c. It abounds in the lava-fissures of volcanic craters, as instanced especially in the case of the Solfatara near Naples (*Forum Vulcani*), and in the volcano of Popocatepetl in Mexico. Sulphur also occurs native in combination with different metals, forming metallic sulphides, of which the principal are blende, iron-pyrites, copper-pyrites, galena, cinnabar, grey antimony, and realgar. Sulphydric acid occurs in hepatic mineral waters, and among the products of animal decomposition. Sulphurous acid is a frequent constituent of volcanic emanations, and free sulphuric acid is sometimes found in the waters of volcanic neighbourhoods. Gypsum, cœlestin, and heavy spar constitute well-known minerals; and, in addition to gypsum, the sulphates of magnesium and sodium are very common ingredients of mineral waters. Sulphur exists in the protein-compounds of animal and vegetable organisms, in the taurine of bile, in the cystin of urine, and in the alliaceous volatile oils.

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* Obtained in needle-shaped crystals by dissolving nitrato-diazobenzoic acid (iv. 294) in sulphuric acid diluted with an equal bulk of water, then adding 3 vols. alcohol and afterwards ether. When heated somewhat above 100°, it is resolved into sulphuric acid, sulphoxybenzoic acid, and a very permanent sulpho-acid, $C^{14}H^{10}SO^8$, which is insoluble in water. (Griess.)

Extraction.—1. Native sulphur is sometimes purified by a rough process of fusion, effected on the spot where it is obtained. A heap is set fire to, whereby the heat evolved from the burning of one portion fuses the remainder. It is more usual, however, to purify it by distillation in upright earthen pots or retorts, set back to back, in two rows, in a long brick furnace. The distillate is received in somewhat similar pots, arranged in two rows outside the furnace, and furnished each with an opening near its base, through which the sulphur condensed within the pot, flows into a pail of water, in which it congeals. The sulphur thus purified by fusion or distillation is known as rough sulphur, and contains about 3 per cent. of foreign matter. It is further purified by redistillation in an iron still. The vapours are sometimes received in a large brick chamber, within which the sulphur condenses in a pulverulent state to constitute flowers of sulphur, or sublimed sulphur; or it is condensed in the liquid state in a smaller and hotter receiver, and is either cast into sticks, when it constitutes roll-sulphur, or is allowed to congeal in mass, when it constitutes refined lump-sulphur.

2. From *Pyrites.*—Sulphur may be obtained by heating disulphide of iron in close vessels, precisely as oxygen is obtained by heating dioxide of manganese under similar conditions:

$$3FeS^2 \quad = \quad Fe^3S^4 \ + \ S^2.$$

Manufactured sulphur is made principally from copper-pyrites, a double sulphide of copper and iron, as a preliminary stage in the process of copper-smelting. Upon a layer of broken pyrites is placed a layer of brushwood, and on this is constructed a huge pyramidal pile of ore, having a central wooden chimney communicating with air-passages left among the brushwood. The whole pile is covered with powdered ore, and the mass set fire to by dropping lighted faggots through the chimney. As the slow combustion of the pile proceeds, sulphur gradually trickles down, and is collected in cavities made extempore in the walls of the heap, whence it is ladled out into moulds. Such a heap, consisting of some 2,000 tons of ore, will continue burning for five or six months, and will yield about 20 tons of rough sulphur, which may be purified by fusion or distillation. Copper-pyrites is sometimes roasted for the extraction of sulphur in a tall-domed furnace, from the summit of which a horizontal flue conveys the sulphur-vapours into a chamber, within which they are condensed. The sulphur obtained from pyrites is partly expelled by heat, partly displaced by oxygen.

3. Sulphur is also prepared in this country from the decomposition, by exposure to air, of the *hydrated sulphide of iron*, resulting from the purification of crude coal-gas with ferric oxide or hydrate:

$$2FeS \ + \ H^2O \ + \ O^3 \quad = \quad 2HFe'''O^2 \ + \ S^2.$$

The hydrate of iron produced in the above reaction is again used to purify the crude gas, whereby it becomes converted into sulphide, and this sulphide is then reconverted into oxide and sulphur by exposure to air as before. These alternate processes are repeated an indefinite number of times, until the amount of sulphur in the material reaches from 40 to 50 per cent., when it is distilled off in iron retorts.

4. From *Alkali-waste.*—Alkali-makers' waste, or tank-waste, consists of sulphide of calcium, together with alkaline sulphides, chalk, lime, &c. (p. 324). This, when decomposed by hydrochloric or carbonic acid, yields a mixture of sulphydric acid and carbonic anhydride; and by introducing an additional quantity of carbonic anhydride, with some atmospheric air or sulphurous anhydride, and heating this mixture of gases to redness, the hydrogen of the sulphydric acid unites with oxygen, forming water, and the sulphur is liberated in the form of uncombined sulphur-vapour, which by cooling becomes condensed to liquid and solid sulphur. (For details of this and the other methods of preparing sulphur, see Richardson and Watts's *Chemical Technology*, vol. i. part iii. pp. 1–27.)

5. Sulphur results from a great number of other reactions, which, however, are not usually employed for its commercial preparation. Thus it may be obtained by decomposing an alkaline polysulphide with an acid; by the decomposition of the chlorides of sulphur with water; by the spontaneous decomposition of hyposulphurous acid; by the ignition of the tri-, tetra-, and penta-thionates, &c.

Properties.—At ordinary temperatures sulphur is a very brittle solid, of a lemon-yellow colour, tasteless from its insolubility in water, and almost inodorous. It is a bad conductor of heat, and a non-conductor of electricity. By friction with wool or hair, it becomes negatively electric. Its specific gravity in the native crystalline state is 2·05. It begins to melt at 114·5°, and at 120° is converted into a perfectly limpid, pale-yellow liquid, which is lighter than solid sulphur. Provided the temperature of 120° has not been much exceeded, it resolidifies suddenly at that same temperature into a transparent mass, which retains its transparency for a long time. By heating sulphur to a temperature much above 120°, its congealing-point is lowered to 111·5°, from the production of a peculiar modification of the element. Sulphur which has been congealed at this low temperature is at first transparent, but becomes opaque much more rapidly than that which has been congealed at 120°. As melted sulphur is gradually heated above 120°, it becomes darker and more viscid, until, at the temperature of 200—250°, it is so thick that the flask in which it is contained may be inverted without any outflow taking place. The temperature of maximum viscidity remains constant for some time, owing to a considerable absorption of latent heat. At from 250—300° and upwards, the sulphur again liquefies, but does not become so fluid as at 115—120° when first melted. On cooling it passes inversely through the same changes of state. Sulphur boils at 440°, and is converted entirely into an orange-coloured vapour. According to Bineau, whose statement has recently been confirmed by Deville and Troost, the density of sulphur-vapour, when taken at the temperature of 1000°, is 32 times as great as that of hydrogen at the same temperature; but its density taken at about 500° is anomalous, being three times as great as it should be theoretically. Sulphur vaporises to a slight extent at ordinary temperatures; so that a piece of silver-leaf, suspended at some distance above a stick of sulphur, becomes slowly transformed into sulphide of silver.

Sulphur is remarkable for the great number of allotropic forms in which it can exist. Of these, however, there are two principal well-characterised varieties, namely, the soluble and insoluble, and many minor modifications. Berthelot distinguishes the soluble variety by the name of electro-negative sulphur, because it is the form which appears at the positive pole of the battery during the electrolysis of sulphydric acid, and is separated from the combinations of sulphur with the electro-positive metals.

Fig. 782.

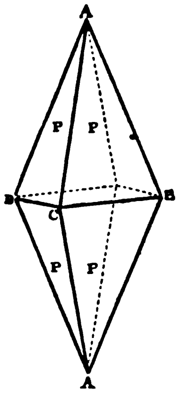


Fig. 783.

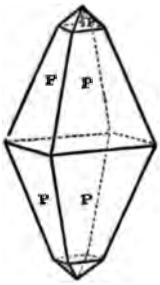
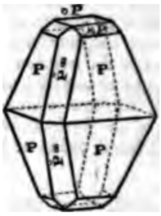


Fig. 784.



The insoluble variety he distinguishes as electro-positive sulphur, because it is the form which appears at the negative pole during the electrolysis of sulphurous acid, and separates from the compounds of sulphur with the electro-negative elements, chlorine, bromine, oxygen, &c. The following are the most important modifications of soluble sulphur:—

1. The *octahedral* variety, frequently represented by the symbol Sα, which is the most stable, and the one into which all the other varieties, soluble or insoluble, tend to change. It is the form in which native sulphur is found, and in which the crystals of sulphur, obtained by the spontaneous evaporation of its solution in carbonic disulphide, are usually deposited. Its specific gravity is 2·05, and its melting-point, according to Brodie, 114·5°. It is readily soluble in carbonic disulphide, disulphide of chlorine, benzene, turpentine, petroleum, &c.; slightly soluble in alcohol and ether. Its crystalline form is that of an elongated octahedron, belonging to the trimetric or right prismatic system (*fig.* 782), with the modifications shown in *figs.* 783, 784. Axes, $a : b : c = 0·8106 : 1 : 1·898$. Angle, P : P (brach.) = 106° 18′; P : P (macr.) = 84° 58′; P : P (basal) = 143° 17′; P̆∞ : P̆∞ (basal) = 124° 24′. Cleavage imperfect parallel to P and ∞P.

2. The *monoclinic* or *oblique prismatic* variety, often represented by the symbol Sβ, may be obtained by the slow cooling of melted sulphur, or by heating octahedral sulphur for some time to a temperature of 105—115°. If, when a few pounds of melted sulphur have been allowed to cool slowly, until a crust has formed on the surface, that superficial crust be broken, and the still liquid sulphur be poured out from the interior, the solidified walls will be seen to be lined with transparent yellowish-brown needles, crystallised in secondary forms of a monoclinic prism. Axes, $a : b : c = 1{\cdot}004 : 1 : 1{\cdot}004$. Angle $b : c = 84° 14'$; $\infty P : \infty P$ (orthod.) $= 89° 28'$; $[P\infty] : [P\infty]$ (clin.) $= 90° 18'$; $oP : \infty P = 85° 54'$. Ordinary combination $\infty P \,.\, oP$ (like *fig.* 284, ii. 152), with $-P$, $[P\infty]$ and $\infty P\infty$. Twins occur combined by the face $\infty P\infty$. The specific gravity of prismatic sulphur is 1·98. According to Brodie, when free from plastic sulphur, the presence of which lowers its melting-point to 111·5°, it melts and resolidifies at 120°. It dissolves readily in carbonic disulphide and other menstrua. In the course of a few days, this prismatic form of sulphur becomes spontaneously converted into the octahedral variety, the conversion being attended with a development of heat, which is most evident when the change is effected artificially by scratching the crystals. Opaque yellow spots first make their appearance, and then gradually spread throughout the mass. The crystals retain their prismatic shape, but on examination are found to be converted into aggregations of minute octahedrons. Conversely, a transparent crystal of octahedral sulphur, when heated to 105—115°, becomes transformed into an opaque mass of oblique prismatic crystals. When a saturated solution of sulphur in hot turpentine is allowed to cool, the crystals first deposited are of the prismatic, those last deposited (when the liquid has become comparatively cool) of the octahedral variety. Occasionally a few transparent, oblique prismatic crystals are deposited from the solution of sulphur in carbonic disulphide, but they soon break up into opaque aggregations of minute octahedrons. Roll-sulphur when first cast is of the oblique prismatic, but by keeping it changes into the octahedral variety. Its molecular condition, however, is unstable, like that of unannealed glass, whence it retains for a long time the specific gravity of the prismatic modification.

3. The *amorphous soluble* variety of sulphur is precipitated, in the form of white emulsin, on addition of acids to diluted solutions of alkaline polysulphides:

$$K^2S^5 + 2HCl = 2KCl + H^2S + S^4.$$

When examined microscopically, it is found to consist of minute granules devoid of crystalline character. It is readily soluble in carbonic disulphide and other menstrua. This form of sulphur has a greenish-white colour, and is known familiarly by the name of "milk of sulphur." By keeping, it becomes gradually converted into octahedral crystals. Sublimed sulphur appears to be allied to this form. It consists of much larger granules, neither the surface nor the fracture of which is crystalline. Sublimed sulphur always contains a minute proportion of one of the insoluble modifications of the element. Vapour of sulphur, when suddenly cooled by contact with a cold surface, condenses in the form of utricles, or of liquid drops surrounded by solid pellicles. These often retain their liquidity for a considerable time, but, when solidified, seem to have the same character as the granules of sublimed sulphur. By keeping they become crystalline in the octahedral form.

The principal modifications of insoluble sulphur are the following:—1. The *amorphous insoluble* variety, the most stable form of which is obtained as a soft magma, by decomposing disulphide of chlorine with water:

$$2S^2Cl^2 + 3H^2O = 4HCl + H^2S^2O^3 + S^2.$$

The hyposulphurous acid produced in the reaction is gradually decomposed into sulphurous acid and sulphur, thus: $H^2S^2O^3 = H^2SO^3 + S$. The sulphur, resulting in this way from the spontaneous decomposition of hyposulphurous acid, has the same characters as those formed by the original decomposition of the disulphide of chlorine. It may be obtained at once by adding dilute hydrochloric acid to the solution of a hyposulphite. If, in preparing amorphous soluble sulphur by adding an acid to the solution of an ordinary alkaline polysulphide containing some hyposulphite, any excess of acid be added, some of this insoluble variety will also be precipitated. The above form of sulphur has a yellow colour, is insoluble in carbonic disulphide or other menstruum, and is quite amorphous. Closely allied to it are the amorphous insoluble sulphur obtained by exhausting sublimed sulphur with carbonic disulphide and alcohol, and that obtained by exhausting reconverted plastic sulphur with carbonic disulphide. This last is a buff-coloured powder, slightly soluble in anhydrous alcohol. Its specific gravity is 1·95. These varieties are convertible into octahedral sulphur by fusion, or by exposure, for a greater or less length of time, to the temperature of 100°.

2. *Plastic* sulphur, frequently represented by the symbol Sγ, is obtained by heating melted sulphur to the temperature 260—300°, and then cooling it suddenly by pouring

it in a very thin stream into cold water. It is thus obtained as a soft, yellowish-brown, semitransparent mass, capable of being drawn out into fine elastic threads possessed of considerable tenacity. This sulphur has a specific gravity 1·95, and is insoluble in carbonic disulphide. When sulphur heated to 300° is suddenly cooled by a mixture of solid carbonic anhydride and ether, it solidifies into a hard perfectly transparent mass, which becomes soft and elastic at ordinary temperatures. This appears to be the solid state of plastic sulphur. Another form of plastic sulphur may be obtained by acting upon metallic sulphides with boiling nitric or nitromuriatic acid. Ordinary plastic sulphur gradually returns in the course of a few hours to its brittle state, reacquires its yellow colour, and becomes converted almost entirely into the octahedral variety, the conversion being accompanied by evolution of heat. If plastic sulphur be heated to 100°, the change takes place suddenly, and the temperature rises to 110°. According to Brodie, sulphur begins to pass into the plastic state at a temperature very little above 120°; and the gradual loss of transparency in crystallised prismatic sulphur depends upon the hardening of plastic sulphur enclosed mechanically between the crystals. Sulphur which has been converted from the plastic into the brittle state does not dissolve entirely in carbonic disulphide, but, as before observed, leaves a buff-coloured residue of insoluble sulphur, the proportion of which may, it is said, be increased by frequently causing the same sulphur to assume alternately the plastic and the brittle state.

The black and red modifications of sulphur, described by Magnus to result, the former from exhausting, with carbonic disulphide, the mass produced by the frequent alternate strong heating and sudden cooling of sulphur, and the latter from heating the black modification to a temperature of 130—150°, are considered by Mitscherlich to depend upon the presence of greasy impurities in the sulphur. When solutions of sulphydric acid and ferric chloride are mixed together, a blue precipitate is sometimes formed, which is said to be a peculiar allotropic form of sulphur.

Sulphur may be made to combine directly with the great majority of the elements. Hydrogen-gas and sulphur-vapour burn in one another, though not very readily, to form sulphydric acid, H^2S. When molted sulphur is treated with chlorine-gas, disulphide of chlorine, Cl^2S^2, is produced, and similar reactions take place with bromine and iodine. Sulphur is highly inflammable, and when heated in air or oxygen to a temperature of 250°, takes fire, and burns with a clear blue, feebly luminous flame, being converted into sulphurous oxide, SO^2. Carbonic disulphide, CS^2, results from passing sulphur-vapour over red-hot charcoal. Sulphur also unites directly with phosphorus, arsenic, silicon, and boron. Nearly all the metals combine directly with sulphur, either at ordinary or increased temperatures. Zinc, iron, copper, lead, silver, tin, &c., burn in sulphur-vapour with great brilliancy, the combustion, save of the zinc and iron, commencing spontaneously, provided the metal is in a sufficiently divided state. Moreover, mixtures of sulphur, water, and finely-divided metal—iron or copper, for instance—begin to react at ordinary temperatures, evolve a considerable amount of heat, and yield hydrated protosulphide. Sulphur, when acted on by strong nitric or nitromuriatic acid, at a gentle heat, is gradually dissolved, with production of sulphuric acid, H^2SO^4. Caustic alkalis also dissolve sulphur readily, with formation of metallic sulphydrate and hyposulphite, thus:

$$4KHO + S^4 = 2KHS + H^2O + K^2S^2O^3.$$

The two atoms of sulphydrate thus produced are capable of dissolving four additional atoms of sulphur to form a metallic pentasulphide and sulphydric acid: $2KHS + S^4 = K^2S^5 + H^2S$.

Sulphur in its chemical relations is the representative of oxygen, to which it is equivalent, atom to atom. The two elements, though very dissimilar in their ordinary physical characters, correspond very closely in the nature of the compounds which they form, and in the properties they exhibit when both are in the gaseous state. Although sulphur rarely, if ever, displaces oxygen by direct elementary substitution, yet the two elements are mutually interchangeable by double decomposition of their respective compounds; and in the great majority of instances where oxygen-compounds are obtainable by addition of oxygen, analogous sulphur-compounds are obtainable by the addition of sulphur. Thus, when cyanide of potassium, KCN, is treated with peroxides, we obtain oxycyanate of potassium, KCNO; and by treating it with sulphur, or persulphides, we obtain sulphocyanate of potassium, KCNS. Again, oxygen-gas and sulphur-vapour alike support the combustion of hydrogen, charcoal, phosphorus, and the metals, to form precisely analogous compounds. The following are a few illustrations of the number and variety of corresponding compounds to which oxygen and sulphur respectively give origin:

$$KHO,\quad CO^2,\quad C^2H^6O,\quad Cl^3PO,\quad K^3PO^4,\quad Sb^2OS^2,\quad K^2SnO^3,\quad \&c.$$
$$KHS,\quad CS^2,\quad C^2H^6S,\quad Cl^3PS,\quad K^3PO^3S,\quad Sb^2S^3,\quad K^2SnS^3,\quad \&c.$$

An atom of sulphur, being the equivalent of an atom of oxygen, is necessarily the equivalent of two atoms of hydrogen or chlorine. Thus the chloride and sulphide of triethylphosphine, Et^3PCl^2 and Et^3PS respectively, made by acting upon triethylphosphine, Et^3P, by chlorine and sulphur respectively, are the strict representatives of one another, and so in other instances. Certain sulphur-compounds, moreover, manifest a great resemblance to those of carbon. (Odling's *Manual of Chemistry.*)

SULPHUR, BROMIDES OF. Sulphur dissolves in bromine at ordinary temperatures without perceptible evolution of heat, and forms a brown-red liquid, containing, according to Löwig, the compound Br^2S^2, which is decomposed by distillation, half of the sulphur being separated, and the compound Br^2S distilling over. Neither of these compounds has, however, been obtained in definite form, as they appear to be capable of dissolving both sulphur and bromine—the latter, indeed, in all proportions. The brown-red solution of sulphur in bromine smells like disulphide of chlorine, and reacts in a similar manner with water, nitric acid, ammonia, &c. (Gm. ii. 283.)

SULPHUR, CHLORIDES OF, or **SULPHIDES OF CHLORINE.** Sulphur and chlorine unite directly even at ordinary temperatures, more quickly, however, when sulphur is sublimed in an atmosphere of chlorine. Only one compound of these elements has been obtained pure in the free state—viz. the disulphide of chlorine, Cl^2S^2, analogous to disulphide of hydrogen. — A protosulphide of chlorine, Cl^2S, analogous to sulphydric acid, is usually described as produced by treating the disulphide with excess of chlorine; but, according to the recent experiments of Carius, it is merely a mixture of the disulphide with the hemisulphide of chlorine, or tetrachloride of sulphur, Cl^4S. This last-mentioned compound is not known in the free state, but exists, according to H. Rose, in combination with several metallic chlorides.

Disulphide of Chlorine, Cl^2S^2. *Protochloride of Sulphur. Halb-Chlorschwefel. Chlorschwefel im Minimum.*—This compound was first described in 1804 by Thomson (Nicholson's Journal, vi. 96), and by Berthelot (Mém. d'Arcueil, i. 161)—the mutual action of chlorine and sulphur having been previously noticed by Hagemann, in 1781—and has been more particularly examined by H. Rose (Pogg. Ann. xxi. 431; xxiv. 303; xxvii. 107; xlii. 517, 542), Dumas (Ann. Ch. Phys. xlix. 204), Marchand (J. pr. Chem. xxii. 507), Heintz (Ann. Ch. Pharm. c. 370), and Carius (*ibid.* cvi. 291; cx. 209).

Disulphide of chlorine is prepared by passing dry chlorine-gas into a retort in which sulphur is sublimed at a gentle heat. It then distils over, and may be collected in a receiver surrounded by cold water, and freed from excess of sulphur by rectification. —It is also produced by distilling a mixture of 1 pt. sulphur with 9 pts. stannic chloride, or 8·5 pts. mercuric chloride. (Berzelius.)

Disulphide of chlorine is a mobile reddish-yellow liquid, having a peculiar, penetrating, disagreeable odour, and fuming strongly in the air. Specific gravity = 1·687. Boils at 139° (Marchand), at 136° (Chevrier, Compt. rend. lxiv. 304). Vapour-density, obs. = 4·77 (Marchand); calc. = 4·68.

It dissolves in carbonic disulphide, alcohol, and ether, not however without decomposition in the two latter. It dissolves sulphur in large quantities, especially when heated. When saturated with sulphur at ordinary temperatures, it forms a clear yellow liquid of specific gravity 1·7, and containing altogether 66·7 per cent. sulphur. The solution of disulphide of chlorine with excess of sulphur in crude benzol, is used for vulcanising or sulphurising caoutchouc.

Reactions.—1. With chlorine, bromine, and iodine.—When *chlorine-gas* is passed for several days in the dark through disulphide of chlorine, a dark brown-red liquid is formed, from which (according to Davy, Dumas, and Marchand) a certain quantity of chlorine may be expelled by gentle ebullition, leaving the protosulphide of chlorine, Cl^2S, which boils constantly at 64°. According to Carius, on the other hand, the boiling-point continually rises during the distillation, and does not become constant till it has risen to 138°, at which temperature disulphide of chlorine passes over. The brown-red liquid is also converted into the reddish-yellow disulphide by passing a stream of dry air through it. At a certain stage of the distillation, a dark brown-red liquid passes over, containing sulphur and chlorine in the proportion required by the formula Cl^2S; but it acts with metals and other bodies like a mixture of the compounds Cl^2S^2 and SCl^4. Hence Carius concludes that the so-called protosulphide of chlorine (or dichloride of sulphur) is not a definite compound, but a mixture, in atomic proportions, of the two compounds just mentioned: $Cl^2S^2 + SCl^4 = 3Cl^2S$. Carius has further shown that, by passing dry chlorine through the disulphide of chlorine at various temperatures, liquids are produced, containing various proportions of sulphur and chlorine, both above and below those required by the formula

In the first case, however, the occurrence of the sulphurous chloride, $SOCl^2$, is, for the most part, masked by the formation of secondary products, as of sulphurous anhydride—thus:

$$SOCl^2 + C^7H^5O.Na.O = NaCl + C^7H^5OCl + SO^2.$$

Acetate of sodium is decomposed by tetrachloride of sulphur in the same manner as the benzoate, but the chloride of acetyl produced acts on another portion of the sodic benzoate, forming acetic anhydride.

The compounds of tetrachloride of sulphur with metallic chlorides are obtained, for the most part, by passing chlorine-gas over the respective sulphides.—The *aluminium-compound*, $2AlCl^3.SCl^4$, is produced by gently heating chloride of aluminium with disulphide of chlorine, and passing chlorine over the resulting dark-red mass at a somewhat higher temperature. A yellow oily liquid is thus obtained, which ultimately solidifies to a crystalline mass. It is decomposed by water, with great evolution of heat, yielding free sulphur, alumina, hydrochloric, sulphuric, and hyposulphurous acids (R. Weber, Pogg. Ann. civ. 421).—The *antimony-compound*, $2SbCl^5.3SCl^4$, obtained by heating grey sulphide of antimony in a stream of chlorine, is a white amorphous powder, which melts when heated, and is resolved into disulphide of chlorine, free chlorine, and trichloride of antimony. It is oxidised and dissolved by nitric acid, and absorbs ammonia in somewhat considerable quantity (H. Rose, Pogg. Ann. xlii. 532).—The *tin-compound*, $SnCl^4.2SCl^4$, produced by the action of chlorine on stannic sulphide, forms fine large crystals, which fume strongly in the air; may be fused and sublimed without decomposition; are gradually dissolved by nitric acid, with formation of stannic oxide and sulphuric acid; form with water an acid liquid, milky from separated sulphur; and absorb ammonia-gas, with considerable evolution of heat, forming a yellow-brown mass which is decomposed by water (H. Rose, Pogg. Ann. xlii. 517).—A *titanium-compound* of uncertain composition, but apparently containing less than 2 at. SCl^4 to 1 at. $TiCl^4$, is produced by mixing titanic chloride with brown chloride of sulphur, or by passing chlorine-gas over titanic sulphide. The first process yields it in large yellow crystals; the second only as a crystalline mass. It deliquesces rapidly in contact with the air, melts when heated, solidifies in the crystalline state on cooling, and sublimes without decomposition. (H. Rose, *ibid.* p. 527.)

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SULPHUR, DETECTION AND ESTIMATION OF. 1. *Reactions.*—The most important compounds in which sulphur occurs are the metallic sulphides, sulphates, sulphites and hyposulphites, and certain organic compounds.

Most metallic sulphides are insoluble in water; those of the alkali-metals and alkaline earth-metals, however, dissolve in water—the former undecomposed, the latter with partial decomposition (p. 483). The solutions give with lead-salts, &c., the reactions of sulphydric acid (i. 217; iii. 204). Sulphides heated on charcoal in the oxidising blowpipe-flame give off all their sulphur as sulphurous anhydride, which may be detected by its odour; or if the sulphide be heated in an inclined glass tube open at both ends, so that a current of air may pass over it, sulphurous anhydride will also be formed, and may be detected by its odour, acid reaction, &c. (p. 540). On fusing a sulphide on charcoal with sodic carbonate or a mixture of that salt and borax, placing the piece of charcoal containing the fused mass on a plate of polished silver, and moistening it, a black or brown stain of sulphide will be formed on the metal. Metallic sulphides, acted upon by strong nitric or nitromuriatic acid, are rapidly oxidised, forming metallic oxide or chloride, sulphuric acid, and usually some free sulphur, which melts into globules very difficult to oxidise.

Metallic sulphates are, for the most part, easily soluble in water; the sulphates of strontium, calcium, lead, and mercurosum are but slightly soluble, and the barium-salt is almost insoluble in water, and likewise in hydrochloric and nitric acid. In soluble sulphates, therefore, sulphuric acid is easily detected by addition of chloride or nitrate of barium, which forms a precipitate insoluble in acids. In insoluble or sparingly soluble sulphates, the sulphuric acid is detected by boiling the salt with a concentrated solution of an alkaline carbonate, whereby an alkaline sulphate is formed, which dissolves in the water. Sulphates heated before the blowpipe on charcoal with sodic carbonate, yield sulphide of sodium, in which the sulphur may be detected in the manner above mentioned. (See SULPHATES).

The sulphites of the alkali-metals are soluble in water; the rest are insoluble or sparingly soluble, but dissolve in excess of sulphurous acid. Sulphites are easily detected by the characteristic odour of sulphurous anhydride, which they evolve when treated with hydrochloric or, better, with dilute sulphuric acid. Hyposulphites treated in the same way also give off sulphurous anhydride, but are distinguished from sulphites by likewise yielding a deposit of sulphur. (See SULPHUR, OXYGEN-ACIDS OF.)

According to W. F. Barrett (Phil. Mag. [4] xxx. 321), sulphur in the free state, and in certain states of combination, may be detected in solids, and in some liquids, by directing a flame of pure hydrogen upon a point of the surface, whereupon, if sulphur is present, even in very minute quantity, a deep blue luminous ring will be formed round the heated point. This effect is produced with free sulphur, with all metallic sulphides, with sulphuric acid, and certain sulphates, especially alum (probably in consequence of reduction), but not with sulphate of sodium and certain others. By this method sulphur has been detected in atmospheric dust.

2. *Quantitative Estimation and Separation.*—Sulphur is almost always estimated in the form of sulphuric acid. To determine the quantity of sulphur in a metallic sulphide, the compound is heated with *nitric* or *nitromuriatic acid*, or sometimes with a mixture of hydrochloric acid and potassic chlorate, till the metal is oxidised, and the sulphur converted into sulphuric acid. The solution is then treated with chloride or nitrate of barium, and the precipitated sulphate of barium is collected on a filter, washed, dried, and ignited. Before adding the baryta-solution, however, the liquid must be considerably diluted with water, because the nitrate and chloride of barium are themselves insoluble in strong nitric and hydrochloric acids. The liquid is then boiled, and afterwards left to stand till the precipitate has completely settled down; after which the clear liquid is first passed through the filter, and then the precipitate thrown upon it; if the precipitate be poured upon the filter before it has settled down, it will be sure to run through. As the oxidation of the sulphur is very slow, the metal being completely oxidised and dissolved long before it, and a portion of the sulphur separated in the free state, it is sometimes convenient to collect this portion on a small weighed filter, determine its amount by direct weighing, and afterwards estimate the dissolved portion as above. The nitric or nitromuriatic acid used for the oxidation should be strong, and the action aided by heat; otherwise, especially in treating the sulphide of manganese, the lower sulphides of iron, and the sulphides of the alkali-metals, part of the sulphur may be driven off as sulphydric acid, and thereby lost. For the same reason, on oxidising with chlorate of potassium and hydrochloric acid, the acid must not be poured at once on to the pulverised sulphide, but gradually added to the mixture of the sulphide with the chlorate of potassium. In applying these methods of oxidation to the sulphides of the alkali-metals and alkaline earth-metals, part of the sulphur is sure to escape as sulphydric acid, unless very particular precautions are taken. The only sure method of guarding against this source of error is to place the sulphide in a small test-tube enclosed in a capacious flask, pour fuming nitric acid upon it, and immediately close the vessel with a tight-fitting stopper.

Another general method of analysing metallic sulphides is, to fuse them with 3 pts. of *potassic* or *sodic nitrate*, and about the same weight of *sodic carbonate*, whereby the sulphur is converted into sulphuric acid, which unites with the alkali, and the metals are converted into oxides. The fused mass is digested with water; the filtered solution neutralised with nitric acid; the sulphur precipitated therefrom as sulphate of barium; and the residual oxides dissolved in hydrochloric or nitric acid.

By the methods just described, the metals are obtained in solution as nitrates or chlorides, and may be separated and estimated by the methods proper for each. Certain special cases may here be noticed. Native sulphide of lead (galena), if not mixed with other sulphides, is best analysed by treating the finely pulverised mass with fuming nitric acid, whereby the lead-sulphide is completely converted into sulphate, and weighing the latter. If, however, other sulphides are present, it is best to fuse the mineral with saltpetre. The use of hydrochloric acid and chlorate of potassium is not advisable, because chloride of lead would be formed as well as sulphate.—Sulphide of bismuth must be oxidised with pure nitric acid, because the presence of hydrochloric acid interferes with the quantitative estimation of bismuth.—Sulphide of silver must also be oxidised with pure nitric acid, and the silver first precipitated from the solution as chloride, then the sulphur from the filtrate as sulphate of barium.

The analysis of fahl-ores, which contain sulphide of arsenic or antimony, or both, in combination with one or more of the sulphides of copper, silver, mercury, iron, and zinc, is generally effected by the following method. The finely powdered mineral is introduced into a double bulb-tube, one end of which is bent at a right-angle, care being taken that all the mineral is contained in the bulb which is farthest from the bent end. The straight end of the tube is then connected with an apparatus for the evolution of perfectly dry chlorine; and the bent end is introduced air-tight into a receiver—which may be a large U-tube—containing a mixture of dilute hydrochloric and tartaric acids; a bent tube is connected with the other end of the U-tube, by which the excess of chlorine is conducted into methylated spirit. The bulb-tube should not be attached to the chlorine apparatus, till all the atmospheric air has been driven out of the latter. A very slow stream of chlorine is then passed through the tube, which decomposes the

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By the methods just described, the metals are obtained in solution as nitrates or chlorides, and may be separated and estimated by the methods proper for each. Certain special cases may here be noticed. Native sulphide of lead (galena), if not mixed with other sulphides, is best analysed by treating the finely pulverised mass with fuming nitric acid, whereby the lead-sulphide is completely converted into sulphate, and weighing the latter. If, however, other sulphides are present, it is best to fuse the mineral with saltpetre. The use of hydrochloric acid and chlorate of potassium is not advisable, because chloride of lead would be formed as well as sulphate.—Sulphide of bismuth must be oxidised with pure nitric acid, because the presence of hydrochloric acid interferes with the quantitative estimation of bismuth.—Sulphide of silver must also be oxidised with pure nitric acid, and the silver first precipitated from the solution as chloride, then the sulphur from the filtrate as sulphate of barium.

The analysis of fahl-ores, which contain sulphide of arsenic or antimony, or both, in combination with one or more of the sulphides of copper, silver, mercury, iron, and zinc, is generally effected by the following method. The finely powdered mineral is introduced into a double bulb-tube, one end of which is bent at a right-angle, care being taken that all the mineral is contained in the bulb which is farthest from the bent end. The straight end of the tube is then connected with an apparatus for the evolution of perfectly dry chlorine; and the bent end is introduced air-tight into a receiver—which may be a large U-tube—containing a mixture of dilute hydrochloric and tartaric acids; a bent tube is connected with the other end of the U-tube, by which the excess of chlorine is conducted into methylated spirit. The bulb-tube should not be attached to the chlorine apparatus, till all the atmospheric air has been driven out of the latter. A very slow stream of chlorine is then passed through the tube, which decomposes the fahl-ore, with considerable evolution of heat; and when the bulb containing the mineral has cooled, it is gently heated in order to separate the volatile chlorides, which must be driven beyond the space between the two bulbs. Those elements which are volatilised as chlorides are *sulphur*, *arsenic*, *antimony*, *mercury*, part of the *iron*, (and, if too strong a heat has been applied, some of the *zinc*): those which remain in the bulb as non-volatile chlorides, are *copper*, *silver*, *zinc*, and the greater part of the *iron*.

For the analysis of the volatile chlorides, the bulb-tube is divided between the two bulbs, and the portion containing the sublimate is covered with a wide tube, closed at one end, and moistened on the inside with water, in which position it is left for 24 hours. The sublimate thus absorbs water gradually, and may then be dissolved out by water, without the evolution of heat and probable loss which would ensue if this precaution were neglected. The tube being thoroughly rinsed out, the solution is added to the liquid in the receiver, any sulphur that separates is filtered off, and any antimony that separates is dissolved by heat. The acid solution is then saturated with sulphydric acid, the washed precipitate digested with sulphide of ammonium, and the undissolved sulphide of mercury collected on a filter, dried at 100°, and weighed ($Hg''S : Hg = 29 : 25$). The sulphides of antimony and arsenic are precipitated from the sulphide of ammonium solution by dilute sulphuric acid, and the metals separated in the manner described under ARSENIC (i. 368). The filtrate (containing tartaric acid) is neutralised with ammonia; sulphide of ammonium added; the precipitated sulphide of iron filtered off, washed with water containing sulphydric acid, and dissolved in hydrochloric acid; the solution heated with nitric acid; and the iron precipitated by ammonia.

The bulb containing the non-volatile chlorides is digested with dilute hydrochloric acid, till only chloride of silver remains undissolved; this is weighed as described at p. 298. From the solution the copper is precipitated by sulphydric acid; and the iron and zinc are separated as described under IRON (iii. 386).

The sulphur is best estimated, in a separate portion of the ore, by fusion with 8 pts. chlorate of potassium and 3 pts. carbonate of sodium.

This mode of analysis is applicable to bournonite (sulphides of antimony, lead, and copper), red silver-ore (sulphides of antimony or arsenic and silver), and other minerals resembling fahl-ores in composition. When *lead* is present, the chlorides must be distilled at a very gentle heat, so that the lead may remain with the non-volatile chlorides; and when these chlorides are treated with dilute hydrochloric acid, a large quantity of water must be added, to insure the complete solution of the plumbic chloride. (Conington's *Handbook of Chemical Analysis*, p. 218.)

The sulphides of the alkali-metals and alkaline earth-metals are sometimes analysed by decomposing them with hydrochloric acid, receiving the evolved sulphydric acid in a solution of acetate of lead, oxidising the precipitated sulphide of lead with fuming nitric acid, weighing the sulphate of lead thus produced, and thence calculating the quantity of sulphur. In the sulphides of gold and platinum, from which the sulphur is completely expelled by ignition, its amount may be determined by weighing the residual metal.

From all non-metallic elements, except selenium and tellurium, sulphur may be separated in the same way as from the metals, viz., by oxidation to sulphuric acid, and precipitation as barium-sulphate. The methods of separating it from selenium and tellurium are given under SELENIUM (p. 225).

The sulphur in organic compounds may likewise be estimated by oxidising the compound with fuming nitric acid, and precipitating the resulting sulphuric acid with a baryta-solution (i. 247). Another method, given by W. J. Russell (Chem. Soc. Qu. J. vii. 212), is to burn the substance in a combustion-tube with oxide of mercury, carbonate of sodium being added to take up the sulphuric acid produced, and a small bent tube dipping under water fitted into the open end of the combustion-tube, so that any acid vapours that escape may be condensed in the water. At the end of the combustion, this liquid is acidulated with hydrochloric acid, the tube washed out with the acid solution, the liquid filtered, and the sulphuric acid precipitated by chloride of barium.

The quantity of sulphuric acid in a soluble sulphate is estimated by precipitating the aqueous solution with chloride of barium. Some sulphates which are insoluble in water, may be dissolved in hydrochloric or nitric acid, and the baryta-solution then added. The sulphates of calcium, strontium, and lead may be decomposed by boiling with a solution of sodic carbonate, and the sulphuric acid precipitated by chloride of barium from the filtered solution previously acidulated with nitric or hydrochloric acid. Sulphate of barium may be analysed by fusing it in a platinum crucible with three times its weight of sodic carbonate; the fused mass digested in water; the filtered soda-solution acidulated; and the sulphuric acid precipitated as above.

Sulphurous and hyposulphurous acid may be estimated by oxidation with nitric acid, whereby they are converted into sulphuric acid; or by Bunsen's iodometric method (i. 265).

3. *Atomic Weight of Sulphur.*—**Berzelius** in 1818 (*Lehrbuch*, v. 1187), determined the atomic weight of sulphur from the quantity of plumbic sulphate ($Pb''SO^4$) produced by treating a known weight of pure lead with nitric and sulphuric acids. 100 pts. of lead yielded from 146·380 to 146·458, or on the average, 146·419 $PbSO^3$: whence (for Pb = 207) S = 32·18. Subsequently (1845), Berzelius obtained nearly the same result by determining the quantity of silver-sulphide produced by decomposing a known weight of the chloride with dry sulphydric acid gas. In four experiments he found (for Ag = 108 and Cl = 35·46), S = 32·1. The same number was found by **Svanberg** and **Struve** (J. pr. Chem. xliv.) from a single experiment made in the same manner. **Erdmann** and **Marchand** in 1844 (J. pr. Chem. xxxi. 396), by heating pure cinnabar in hydrogen gas, obtained from 100 pts. of the sulphide, in four experiments, 86·205 to 86·222 pts., mean 86·211 pts. of mercury: hence (for Hg = 200), S = 32·005. **Struve** in 1852 (Ann. Ch. Pharm. lxxx. 203) by reducing argentic sulphate with hydrogen, obtained, as a mean of six experiments, S = 32. **Dumas** in 1859 (Ann. Ch. Pharm. cxiii. 20), by converting a known weight of silver into sulphide, Ag^2S, obtained S = 32·01; and lastly, **Stas** in 1860 (*Recherches sur les rapports réciproques des poids atomiques*) by heating silver in a stream of pure sulphur-vapour or pure sulphydric acid gas, obtained as a mean of five experiments, from 100 pts. silver, 114·8522 argentic sulphide: whence S = 32·07.

All these results come so near to the whole number 32, that this number may be used in calculation without sensible error.

SULPHUR, FLUORIDE OF. According to Davy and Dumas, a compound of fluorine and sulphur is obtained by distilling fluoride of lead or fluoride of mercury with sulphur.

SULPHUR, IODIDES OF. Iodine and sulphur combine when heated together even under water. The resulting compound, I^2S^2, is a blackish-grey radio-crystalline mass, resembling native sulphide of antimony. It decomposes at higher temperatures, gives off iodine on exposure to the air, and is insoluble in water.—By heating 2 at. iodine with 1 at. sulphur, a compound is obtained which smells like iodine, and is said to be a powerful remedy in skin diseases.—A cinnabar-red iodide of sulphur is obtained, according to Grosourdi, by precipitating trichloride of iodine with sulphydric acid.

SULPHUR, OXIDES AND OXYGEN-ACIDS OF. Sulphur forms two oxides, viz. **sulphurous oxide or anhydride**, SO^2, and **sulphuric oxide or anhydride**, SO^3. Sulphurous oxide is produced by the combustion of sulphur in air or oxygen-gas: and sulphuric oxide may be formed by passing a mixture of dry sulphurous oxide and oxygen or air over heated spongy platinum. Each of these oxides unites with 1 at. water, forming respectively **sulphurous acid**, $H^2O.SO^2 = H^2SO^3$, and **sulphuric acid**, $H^2O.SO^3 = H^2SO^4$.

These two acids may be regarded as oxides of sulphydric acid, H^2S. A complete series of oxidised compounds of sulphydric acid would comprise the following members, corresponding to the oxides of hydrochloric acid (i. 907):

Sulphydric acid,	H^2S.	Hydrochloric acid,	HCl.
————	H^2SO.	Hypochlorous acid,	HClO.
————	H^2SO^2.	Chlorous acid,	$HClO^2$.
Sulphurous acid,	H^2SO^3.	Chloric acid,	$HClO^3$.
Sulphuric acid,	H^2SO^4.	Perchloric acid,	$HClO^4$.

The first and second members of the sulphur series of oxygen-compounds are at present unknown, but we are acquainted with their chloro-derivatives, **sulphurous chloride, or chloride of thionyl**, Cl^2SO, and **sulphuric chloride, or chloride of sulphuryl**, Cl^2SO^2.

The chlorine acids are monobasic, or contain but one atom of replaceable hydrogen; but the sulphur-acids are dibasic, or contain two atoms of hydrogen replaceable by metals; both sulphurous and sulphuric acids are accordingly capable of forming neutral, acid, and double salts.

Sulphurous and sulphuric acids can be formed from the anhydrides by direct hydration, and the anhydrides from the acids by direct dehydration.

Sulphurous and sulphuric acids can both be obtained by the direct oxidation of sulphydric acid; and conversely, metallic sulphides can be formed by the deoxidation of sulphites and sulphates. Sulphurous acid, moreover, very readily affords sulphydric acid by deoxidation.

Sulphurous and sulphuric acids are convertible into one another by oxidation and deoxidation respectively.

Sulphurous and sulphuric chlorides, $SOCl^2$ and SO^2Cl^2, yield sulphurous and sulphuric acids respectively by treatment with water [replacement of Cl^2 by $(HO)^2$], and may be reproduced from those acids by the action of pentachloride of phosphorus. They may also be produced from the chlorides of sulphur (p. 534).

Allied to the sulphates there is a group of salts called thiosulphates or more frequently hyposulphites. Their composition is that of sulphates (M^2SO^4), in which 1 at. oxygen is replaced by sulphur, their general formula being $M^2S^2O^3$. When a sulphite, such as Na^2SO^3, is acted upon by oxygen or a peroxidised substance, it becomes an oxysulphate, Na^2SO^4; when acted upon by sulphur or a persulphuretted substance, it becomes a thiosulphate, $Na^2S^2O^3$.

There is also a remarkable series of acids called polythionic acids containing six atoms of oxygen and two or more atoms of sulphur, viz.:

$H^2S^2O^6$ Dithionic acid.
$H^2S^3O^6$ Trithionic acid.
$H^2S^4O^6$ Tetrathionic acid.
$H^2S^5O^6$ Pentathionic acid.

The corresponding anhydrides are not known.

The dithionates (also called *hyposulphates*) are formed directly from sulphurous anhydride and a metallic peroxide, thus: $MnO^2 + 2SO^2 = Mn''S^2O^6$. When heated they break up into a sulphate and sulphurous anhydride, *e.g.* $Mn''S^2O^6 = Mn''SO^4 + SO^2$. The tri-, tetra-, and penta-thionates undergo a similar decomposition when heated, but yield sulphur in addition.

Sulphurous Compounds.

DIOXIDE OF SULPHUR, SULPHUROUS OXIDE, OR SULPHUROUS ANHYDRIDE, SO^2.—This compound occurs as gas in volcanic neighbourhoods, in the gaseous state and dissolved in the water of the springs. It is formed artificially either by oxidation of sulphur or by deoxidation of sulphuric acid:—(α) By burning sulphur in air or oxygen, by roasting metallic sulphides, or by heating sulphur with metallic oxides, those of copper and manganese for instance; (β) By heating sulphuric acid with copper, mercury, or other metals, or with charcoal, sulphur, or organic bodies. It also results from the decomposition of thiosulphuric and dithionic acids.

Preparation.—Sulphurous oxide is usually prepared by the deoxidation of sulphuric acid. For preparation on the laboratory scale, strong sulphuric acid is heated with copper or mercury:

$$Hg + 2H^2SO^4 = Hg''SO^4 + 2H^2O + SO^2.$$
$$Cu^2 + 2H^2SO^4 = Cu^2SO^4 + 2H^2O + SO^2.$$

The sulphurous oxide then passes off as gas, and the residue consists, in the case of mercury, of mercuric sulphate, in the case of copper, of cuprous sulphate, mixed, according to Maumené, with cuprous and cupric sulphides. The gas may be passed through a small quantity of water to wash it, and then dried over chloride of calcium. In the manufactory, charcoal, straw, sawdust, &c., are substituted for the metals, but the sulphurous oxide obtained by means of these substances is always contaminated with about half its bulk of carbonic dioxide. Wach (Schw. J. l. 26) recommends a laboratory process for making sulphurous oxide, by heating sulphur and sulphuric oxide together in sealed U-tubes, whereby the sulphurous oxide is obtained in the liquid state, at the cooled extremity.

Properties.—At common temperatures, sulphurous oxide is a gas, but it may very readily be condensed into the liquid state by a pressure of three atmospheres, or by a freezing mixture of ice and salt. The liquid oxide may be obtained in large quantities by heating copper turnings with sulphuric acid, and passing the evolved gas first through a little water to wash it, then through an empty U-tube surrounded by ice to cool the gas and condense its moisture, then through a chloride of calcium tube to render it perfectly dry, and lastly into a suitable receiver immersed in a freezing mixture of salt and ice. The product thus obtained may be preserved in sealed tubes, or in soda-water bottles firmly corked and wired, or preferably closed with a vulcanised caoutchouc pad retained by a screw-clamp. When the liquid oxide is evaporated rapidly under the air-pump, or when it is cooled by a mixture of solid carbonic dioxide and ether, it solidifies in white semicrystalline flakes. Solid sulphurous oxide is heavier than the liquid. It melts at about −79°. The liquid oxide is a colourless, transparent, mobile fluid. Its specific gravity is 1·45. It boils at −10°. Respecting the tension of its vapour, as determined by Regnault, see HEAT (iii. 94).

By its evaporation it produces intense cold, sometimes even sufficient to freeze itself, and readily to freeze water on which it is poured.

Sulphurous oxide in the gaseous state is colourless, irrespirable, and incombustible. It is more than twice as heavy as atmospheric air, and may consequently be collected by displacement. It may also be collected over mercury, but not over water, in which it is very soluble. It has a peculiar suffocating sulphurous odour. When perfectly dry it does not redden litmus-paper, at any rate not for some time. It temporarily bleaches many vegetable colours. The oxide or acid is largely used for bleaching wool, straw, &c., and for preserving certain animal tissues, such as vellum and catgut. The moist substances are placed in close chambers in which sulphur is burnt. The colouring-matters seem merely to enter into combination with the acid or anhydride, and may be reproduced by the addition of an alkali to neutralise, or of a stronger acid to expel the sulphurous acid. The fume of burning sulphur has also been employed as a disinfecting agent.

When heated to 1200° or upwards, or subjected to the action of a powerful induction-spark, it is resolved into free sulphur and oxygen, which oxidises part of the sulphurous oxide to sulphuric oxide. It rapidly extinguishes the flame of burning bodies.—Nevertheless *potassium* burns brightly in it, forming a polysulphide of potassium together with sulphate and thiosulphate.—Finely divided *tin* heated in the gas also burns brightly, forming stannic oxide and sulphide.—*Arsenic* acts upon it only in the form of vapour, forming arsenious oxide and sulphide.—*Antimony* is slowly attacked by it, forming the red trisulphide.—Precipitated *lead* is slowly converted into sulphide.—*Iron* (finely divided) glows when heated in the gas, forming sulphide of iron and ferrous sulphate.—*Manganic peroxide*, gently heated in the gas, is converted into manganous sulphate: *lead-oxide* or *carbonate*, chiefly into sulphide.—*Cupric oxide* is two-thirds reduced to cuprous oxide, the remainder being converted into cupric sulphide. (Schiff, Ann. Ch. Pharm. cxvii. 92.)

Sulphurous Acid, $H^2SO^3 = H^2O.SO^2 = \left.\begin{matrix}(SO)''\\ H^2\end{matrix}\right\}O^2$.—*a.* This acid may be obtained by burning sulphydric acid in excess of air or oxygen; or by liberating it from its salts, the sulphites, by the addition of a stronger acid, such as the sulphuric, hydrochloric, oxalic, &c.—In practice it is always made by passing sulphurous oxide into water. When liquid sulphurous oxide is added to ice-cold water, or even to ice, combination attended by violent ebullition takes place, while a solid hydrated acid remains, mixed with an excess of ice, whether used as such or frozen during the reaction. The solid hydrated acid, in the form of white laminated crystals, may also be made by passing moist sulphurous oxide gas through a freezing mixture. Pierre (Ann. Ch. Pharm. lxviii. 228) obtained nitre-like crystals of sulphurous acid, having the formula $H^2SO^3.8H^2O$, by cooling to $-6°$ a saturated solution of sulphurous acid through which a current of the gas was being transmitted. The crystals fused at $+4°$. Döpping (J. pr. Chem. xliv. 255) succeeded in procuring the pure acid, H^2SO^3, in the form of cubical crystals, by cooling to zero a saturated aqueous solution of sulphurous acid.

The solution of sulphurous acid is made commercially by condensing the vapour from burning sulphur in a coke scrubber, through which water is kept trickling. In the laboratory the gaseous oxide is passed into distilled water, which at 15° absorbs about 45 times its volume of the gas (ii. 798). The combination is attended by a slight elevation of temperature. The resulting liquid has a specific gravity of 1·04. It is colourless, has the smell of burning sulphur, and reacts strongly acid to test-paper. When boiled it gives off sulphurous acid or oxide, but very prolonged ebullition is required to drive off the whole of the gas. By exposure to air, the solution slowly oxidises into sulphuric acid. When mixed with hydrochloric acid and metallic zinc or stannous chloride, it is reduced to the state of sulphydric acid, which in the case of zinc may be recognised by its reaction on lead-paper. With stannous chloride a precipitate of brown stannous sulphide is formed.

Sulphurous oxide and sulphurous acid act as powerful reducing agents. They liberate iodine from iodic acid, and, in presence of water, finally convert it into hydriodic acid. The smallest trace of free sulphurous acid in a gaseous mixture, or in a solution, may be detected by means of strips of paper steeped in starch-paste to which a small quantity of iodic acid or potassic iodate has been added. The sulphurous acid sets free the iodine, which forms the well-known blue compound with the starch (Persoz, Ann. Ch. Pharm. lxiv. 408). Starch-paper, containing iodide of potassium, which has been turned blue by the action of chlorine, is decolorised by sulphurous acid. (Schönbein, Pogg. Ann. lxx. 88.)

Sulphurous acid and iodine, in presence of a large quantity of water, yield hydriodic and sulphuric acids: $H^2SO^3 + I^2 + H^2O = 2HI + H^2SO^4$. Bunsen's method of volumetric analysis is based upon this reaction.

Sulphurous acid and oxide reduce the arsenic, chromic, and permanganic acids, and precipitate metallic gold from its chloride. They also precipitate tellurium and selenium from tellurious and selenious acids respectively, and sulphur from sulphydric acid.

For the detection of sulphurous oxide in gaseous mixture, Schiff (Ann. Ch. Pharm. cxviii. 91) recommends the use of paper moistened with solution of mercurous nitrate, which becomes grey from precipitation of metallic mercury. Bright metallic copper heated with hydrochloric acid containing sulphurous acid immediately becomes dull, then grey and brown, or brown-black, from formation of sulphide. The deposit thus formed is distinguished from that produced by arsenic under similar circumstances by not adhering closely to the metal, by not disappearing when heated in a tube, and by not dissolving, with evolution of hydrogen, when boiled with moderately dilute hydrochloric acid. Reinsch (Zeitschr. anal. Chem. i. 220) recommends this reaction as a very delicate test for sulphurous acid; but according to Fresenius (*ibid.* i. 221), it is not nearly so delicate as that with iodate of potassium and starch.

SULPHUROUS CHLORIDE, $SOCl^2$. *Chloride of Thionyl. Sulphurous Chloraldehyde.*—This compound, derived from sulphurous acid, SO.HO.HO, by the substitution of 2 at. chlorine for 2 at. hydroxyl, is formed by the action of water alcohols, acids, &c. on the sulphides of chlorine (pp. 534, 535); but is more easily prepared by the action of phosphoric pentachloride on sulphurous oxide (Schiff, Ann. Ch. Pharm. cii. 111), or by that of phosphoric oxychloride on sulphite of calcium (Carius, *ibid.* lxx. 297):

$$SO^2 + PCl^5 = POCl^3 + SOCl^2.$$

$$3CaSO^3 + 2POCl^3 = Ca^3P^2O^8 + 3SOCl^2.$$

It is separated by fractional distillation from the fixed calcic phosphate produced simultaneously in the second, and by fractional distillation from the phosphoric oxychloride produced in the first reaction.

Sulphurous chloride is a colourless, strongly refracting liquid, which boils at 82°. It is decomposed by water, yielding hydrochloric and sulphurous acids; by alcohols with formation of hydrochloric acid and alcoholic chlorides and sulphites (p. 535), and by ammonia, with formation of thionamide: $Cl^2SO^2 + 2NH^3 = H^2O + (NH^2)^2SO$.

METALLIC SULPHITES.—Sulphurous acid, as already observed, is dibasic, forming normal or neutral, and acid salts represented by the formulæ M^2SO^3 and $MHSO^3$ for monatomic metals; and by corresponding formulæ for polyatomic metals; also double salts. The sulphites have been examined chiefly by Muspratt (Ann. Ch. Pharm. l. 259; lxiv. 240) and Rammelsberg (Pogg. Ann. lxvii. 245, 391).

Sulphites are usually made by transmitting gaseous sulphurous oxide through water in which metallic hydrates or carbonates are dissolved or suspended. The acid sulphites of barium, strontium, calcium, and magnesium, and the neutral and acid sulphites of lithium, sodium, and potassium, are soluble in water. Most other sulphites are insoluble, and may be prepared by precipitation with a sulphite of alkali-metal. The sulphites M^2SO^3 and $MHSO^3$, present a great analogy to, and are for the most part isomorphous with, the carbonates, M^2CO^3 and $MHCO^3$ respectively. Both acid and neutral sulphites form well-defined crystals, sometimes hydrated, but more generally anhydrous. The sulphites are decomposed at a red heat, either into sulphate and sulphide, or into sulphurous anhydride and metallic oxide. When heated with charcoal, they are completely reduced to the state of sulphides, or in some cases to that of oxides. They are also readily reduced in the moist way by stannous chloride, or by nascent hydrogen evolved from hydrochloric acid and zinc, with formation of metallic sulphide or of sulphydric acid. The sulphites, particularly if in solution, become converted into sulphates by exposure to air, or by treatment with oxidising agents, such as nitrous acid, hypochlorous acid, chlorine, &c. The solutions also, when acted on by sulphur, sulphydric acid, or alkaline sulphydrate, form thiosulphates (hyposulphites). The sulphites are decomposed by nearly all acids, save the carbonic and boric, with liberation of sulphurous acid. The acidified solutions of the salts act like sulphurous acid as powerful reducing agents, and are frequently employed as such in analysis. Acid sulphite of sodium was at one time much used as an *antichlore* (i. 310).

Sulphite of Aluminium.—A basic sulphite, $Al^2O^3.SO^2.4H^2O$ or $Al^2(SO^3)^3.4AlH^3O^3.6H^2O$, is obtained, according to Gougginsperg, by dissolving recently precipitated aluminic hydrate in cold aqueous sulphurous acid, or passing sulphurous gas into water in which the hydrate is suspended. On heating the resulting solution, the salt separates as a white earthy powder, which must be collected on a filter while hot, as it redissolves on cooling. It is insoluble in pure water, and on exposure to the air is gradually converted into sulphate.

Sulphites of Ammonium.—The *neutral salt*, $(NH^4)^2SO^3.H^2O$, is prepared by passing sulphurous oxide and ammonia-gases, both moist, into absolute alcohol; the liquid then becomes filled with white silky crystals of the salt, which must be dried between filter-paper. It has a strong alkaline reaction, an unpleasant caustic taste, and dissolves very slowly in water. The crystals, when exposed to the air, first become moist, but afterwards dry, being converted by oxidation into sulphate of ammonium. (Muspratt.)

The neutral sulphite, when heated, gives off water and ammonia, and is converted, according to Muspratt, into the *anhydrosulphite*, $(NH^4)^2O.2SO^2$ or $(NH^4)^2SO^3.SO^2$. [It might rather be expected to yield the *acid sulphite*, $NH^4.H.SO^3 = (NH^4)^2SO^3 - NH^3$]. This salt is neutral to vegetable colours, gives off a considerable quantity of sulphurous oxide on exposure to the air, and is gradually but completely converted into sulphate of ammonium. It dissolves easily in water and in alcohol. When heated in a tube it gives off sulphurous oxide, and yields a sublimate perhaps consisting of $2NH^3.SO^2.\frac{1}{2}H^2O$ or $\left.\begin{matrix}H^2\\(SO)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}.\frac{1}{2}H^2O$. When sulphurous oxide is passed into aqueous ammonia till the odour is entirely destroyed, and absolute alcohol is then added, a white alkaline crystalline mass separates, containing $(NH^4)^2SO^3.NH^3.\frac{3}{2}H^2O$. (Muspratt.)

Sulphite of Antimony, $Sb^2O^3.3SO^2 = \overset{'''}{Sb}{}^2(SO^3)^3$, is obtained, according to Berzelius, by digesting antimonious oxide in sulphurous acid, or by passing sulphurous oxide into antimonious chloride. It is a white insoluble powder.

Sulphite of Barium, $Ba''SO^3$, is obtained by precipitation as a white powder, and crystallises from solution in warm aqueous sulphurous acid in permanent six-sided prisms. When heated in a close vessel, it is resolved, according to Rammelsberg, into sulphide and sulphate of barium: $4BaSO^3 = BaS + 3BaSO^4$.

Sulphite of Bismuth, $Bi^2O^3.SO^2 = 2Bi^2O^3.Bi^2(SO^3)^3$, is deposited, according to Danson, from a solution of bismuth-oxide in the aqueous acid, left to stand in a close vessel, as a straw-yellow precipitate, becoming white when dry. According to Muspratt, it is likewise produced by passing sulphurous oxide through the nitrate.

Sulphite of Cadmium, $Cd''SO^3$.—The anhydrous salt separates from the aqueous solution by evaporation, in indistinct crystalline forms (Rammelsberg). On adding alcohol to the solution, the same salt separates as a precipitate resembling alumina, which, if left to stand in the liquid, changes into fine silvery crystals of the hydrated salt, $Cd(SO^3)^3.H^2O$. these crystals dissolve sparingly in water, easily in dilute acids (Muspratt). The salt oxidises slowly in the air, and when heated, gives off sulphurous oxide, leaving a yellow residue of cadmic oxide, sulphide, and sulphate. Sulphate of cadmium is also formed, together with the sulphide, on dissolving cadmium in sulphurous acid. (Fordos and Gélis.)

Ammonio-cadmic sulphite, $(NH^4)^2Cd''(SO^3)^2$, is obtained, according to Schüler, by passing sulphurous oxide to saturation into the solution obtained by adding ammonia in slight excess to chloride of cadmium. It then separates as a white precipitate consisting of microscopic rhombic prisms, nearly insoluble in water, even on boiling. When heated, it gives off sulphite of ammonium, leaving a mixture of cadmic oxide and sulphate.—*Acid sulphite of Cadmammonium*, $(NH^2Cd'')HSO^3$, is formed by dissolving cadmic sulphite in aqueous ammonia, and separates on cooling as a crystalline powder, or in small shining prisms which smell of ammonia and are decomposed by water. (Rammelsberg.)

Sulphite of Calcium, $Ca''SO^3$, is obtained in the anhydrous state by precipitation. On suspending the precipitate in water, passing sulphurous oxide through the liquid, and leaving the resulting solution for several days over oil of vitriol, a hydrated salt separates in six-sided prisms containing $Ca''SO^3.2H^2O$ (Muspratt), $2Ca''SO^3.H^2O$ (Rammelsberg). Sulphite of calcium has an astringent sulphurous taste, and becomes covered, on exposure to the air, with silky efflorescences of calcic sulphate. When heated, it gives off water, sulphurous oxide, and sulphur, and leaves a residue of calcic sulphide and sulphate (Muspratt, Rammelsberg). Respecting the preparation of this salt on the large scale, and its use in bleaching, and in protecting organic substances from decay, see Anthon. (Dingl. pol. J. clix. 137.)

A compound of *calcic sulphite* and *sulphide*, $CaSO^3.2CaS.6H^2O$, is found, according to Kuhlmann (Compt. rend. lii. 1169), lining the cavities of soda-residues which have been lixiviated, and afterwards exposed to the air for several years.

Sulphite of Cerium, $Ce''SO^3$, crystallises in needles. (Klaproth.)

Sulphite of Chromium, $2Cr^2O^3.3SO^2.16H^2O$, separates from solution as a yellow powder (Danson), on addition of alcohol, or on heating, as a greenish-white powder which gives off sulphurous oxide when heated (Muspratt). According to Berthier, sulphurous oxide passed into a solution of potassic chromate forms a brown precipitate, gradually turning green, and dissolving to a green liquid, which deposits a basic salt on cooling.

Sulphites of Cobalt.—*a. Cobaltous Sulphite*, $Co''SO^3$, separates on addition of alcohol to the solution of cobaltous carbonate in sulphurous acid, as a flocculent precipitate probably containing 1 at. water. From a solution freed from air by boiling and left to cool in a closed vessel, red granular crystals separate containing 5 at. water (Muspratt). The same solution evaporated down in an atmosphere of hydrogen, gives off sulphurous oxide, and deposits peachblossom-coloured crystals of a salt containing 3 at. water. The mother-liquor on cooling deposits a light rose-coloured powder, probably a basic salt. Ammonia partially dissolves the trihydrated salt with red-brown colour, and alcohol added to the solution throws down a yellow crystalline powder containing ammonia, sulphurous oxide, and probably cobaltic oxide, Co^2O^3. (Rammelsberg.)

Potassio-cobaltous sulphite, $K^2O.Co''O.2SO^2 = K^2Co''(SO^3)^2$, is obtained, as a pale-red crystalline or amorphous precipitate, by heating cobaltous sulphite or chloride with neutral sulphite of potassium, or by boiling cobaltic hydrate with a sufficient quantity of the alkaline sulphate.—A *sodium-salt* containing $Na^2O.3Co''O.3SO^2$ or $Na^2\overset{''}{Co}{}^2(SO^3)^3.Co''O$, is prepared in like manner. Both salts oxidise on exposure to the air. (W. Schultze, Zeitschr. Ch. Pharm. 1865, p. 89; Jahresb. 1865, p. 270.)

β. Cobaltic Sulphites.—A warm solution of ammonium-sulphite dissolves recently precipitated cobaltic hydrate, with evolution of ammonia, forming a dark alkaline liquid; and this, if strongly saturated, deposits after a while, a reddish-yellow powder which redissolves on washing with water, the solution then gradually depositing yellow-brown crystals, and afterwards a yellow powder containing $2(Co^2O^3.3SO^2).10NH^3.9H^2O$, and apparently identical with the purpureo-cobaltic sulphite described by Künzel (i. 1049). The mother-liquor deposits brown crystals which are decomposed by water, yielding a yellow salt probably identical with Künzel's triammonio-cobaltic sulphite (i. 1051). (Geuther, Ann. Ch. Pharm. cxxviii. 157; Jahresb. 1863, p. 267.)

Potassio-cobaltic sulphite, $K^2O.Co^2O^3.4SO^2 = KCo'''(SO^3)^2$, is formed, by heating cobaltic hydrate for some time with a frequently renewed, concentrated, neutral, or slightly alkaline solution of potassic sulphite, as an amorphous powder which dissolves slightly in sulphurous or hydrochloric acid, and decomposes in drying.—A *sodium-salt*, having the composition $Na^2O.Co^2O^3.3SO^2$, is obtained in a similar manner. (Geuther, Schultze.)

Sulphites of Copper.—*a.* A basic *cupric sulphite*, $4Cu''O.SO^2.7H^2O$ or $Cu''SO^3.3Cu''H^2O^2.4H^2O$, is obtained by adding cupric hydrate to absolute alcohol saturated with sulphurous oxide, as a green precipitate, insoluble in water, and not decomposed by washing therewith.

β. Cuprous sulphite, Cu^2SO^3.—The anhydrous salt, which has a brown-red colour, is obtained, according to Böttger, by treating cuprous hydrate with aqueous sulphurous acid. The same salt is obtained pure and as a hydrate, by passing sulphurous oxide through water in which ammonio-cuprous sulphite is suspended. The latter is thus converted into an insoluble red powder, which on boiling the liquid, is converted into a mass of microscopic crystals consisting of $Cu^2SO^3.H^2O$, resembling the red double salt in general appearance, but lighter-coloured, and exhibiting under the microscope, distinct quadratic prisms or octahedrons, whereas the double salt crystallises in oblique prisms. Cuprous sulphite is converted by hydrochloric acid into cuprous chloride, and dissolved by ammonia to a colourless liquid which does not turn blue. (Rogojski, J. pr. Chem. liii. 408.)

Ammonio-cuprous sulphite, $(NH^4)CuSO^3$, is obtained in colourless laminæ by decomposing cupric sulphate with excess of ammonium-sulphite, and passing sulphurous oxide through the brown liquid till it becomes colourless; or by passing the sulphurous gas (not too long) through an ammoniacal solution of cupric sulphate (Rogojski); or by adding sulphite of ammonium at the boiling heat to a solution of cupric sulphate or nitrate strongly supersaturated with ammonia, till it becomes colourless; the resulting solution mixed with excess of nitric acid and exposed to the air, deposits the double salt in nacreous six-sided tables (H. Vohl, J. pr. Chem. xcv. 218). It is insoluble in cold water, and is decomposed by boiling water into sulphurous oxide and cuprous oxide; also by sulphuric acid into metallic copper and cupric sulphate. In a solution of cupric sulphate it is immediately converted into red cuproso-cupric sulphite (Rogojski).—Another double salt, containing $Cu^2SO^3.7(NH^4)^2SO^3.10H^2O$ or $(NH^4)^7Cu(SO^3)^4.5H^2O$, is produced, according to Péan-de-Saint-Gilles (Ann.

Ch. Pharm. lxxxviii. 165; Jahresb. 1853, p. 372), by treating cuprous chloride with sulphite of ammonium. It crystallises in needles, and is converted into the preceding salt by saturating its solution with sulphurous acid.

Potassio-cuprous Sulphites.—The salt, $Cu^2SO^3.2K^2SO^3$, is produced, according to Chevreul and Muspratt, by adding sulphite of potassium to a moderately concentrated solution of cupric sulphate or nitrate, or according to Vohl by passing sulphurous oxide into a solution of a cupric salt mixed with excess of potash. It is a yellow precipitate which by boiling with water is converted into the salt $3Cu^2SO^3.3Cu''SO^3.2K^2SO^3$. Rammelsberg, by mixing a cupric salt in the cold with sulphite of potassium, and digesting the resulting yellow-brown precipitate with a strong solution of potassic sulphite, obtained a salt containing apparently $Cu^2SO^3.8K^2SO^3.16H^2O$; but its composition is uncertain, as it was perhaps mixed with uncombined potassic sulphite.

Sodio-cuprous sulphite, $Cu^2SO^3.5Na^2SO^3.38H^2O$, is formed, according to Muspratt, by adding alcohol to a mixture of the solution of sodic and cupric sulphites; on leaving the liquid thereby separated in a vacuum, the double salt is deposited in fine yellow crystals.

A *sodio-ferroso-ferrico-cuprous sulphite*, $\left.\begin{matrix}Na^2O.SO^2\\2(Fe''O.SO^2)\\Fe^2O^3.2SO^2\\Cu^2O.SO^2\end{matrix}\right\}.16H^2O$, is said to be obtained by adding neutral sulphite of sodium to a solution of 2·49 grms. (2 at.) cupric sulphate and 5·56 grms. (4 at.) ferrous sulphate in 100 c.c. water. The precipitate formed at first redissolves to a dark purple-red liquid, which after some hours deposits the complex salt in small black crystals, appearing dark purple-red by transmitted light. (A. Stromeyer, Ann. Ch. Pharm. cix. 237.)

Cuproso-cupric Sulphite, $\left.\begin{matrix}Cu^2\\Cu''\end{matrix}\right\}S^2O^6.2H^2O = Cu^2SO^3.Cu''SO^3.2H^2O$. (Rammelsberg and Rogojski.)—Prepared by treating hydrate or carbonate of copper with aqueous sulphurous acid, or by passing sulphurous oxide through water in which either of these compounds is suspended (Muspratt), or by adding a concentrated solution of acid potassic sulphite to a solution of cupric sulphate, and gently warming the filtered liquid (Bourson). It forms red crystals or a crystalline powder, which dissolves in hydrochloric acid with brown colour, becoming green on dilution, with separation of white cuprous chloride. The same salt is obtained combined with 5 at. water, by slowly passing sulphurous oxide through a solution of cupric acetate, or by adding an alkaline sulphate to a cupric salt in excess. It then separates as a yellow flocculent precipitate, which remains unaltered in dry air, is insoluble in water, but dissolves without decomposition in acetic or sulphurous acid. On evaporating its solution the red dihydrate separates out. (Péan-de-St-Gilles.)

Ammonio-cuproso-cupric sulphite, $(NH^4)^2Cu^2Cu''(SO^3)^3.5H^2O$, separates in light-green crystals on mixing a saturated solution of ammonium-sulphite with cupric sulphate (Péan-de-St-Gilles).—A *potassio-cuproso-cupric sulphite*, $K^4Cu^6\overset{''}{Cu}{}^2(SO^3)^6$, is obtained as a red precipitate on heating a solution of cupric sulphate with potassic sulphite. (Rogojski.)

Sulphite of Didymium, $Di''SO^3.H^2O$.—Produced by passing sulphurous oxide through water in which strongly-ignited oxide of didymium is suspended. The rose-coloured solution becomes turbid when heated, and deposits the salt as a light bulky precipitate, which redissolves on cooling. If, however, the excess of sulphurous acid be expelled by boiling, the precipitate becomes reddish-white and pulverulent, and no longer redissolves on boiling. (Marignac.)

Sulphite of Glucinum, $G''SO^3$, is very soluble in water, and is not decomposed by boiling.

Sulphites of Gold.—Neither auric nor aurous sulphite is known in the separate state.—*Potassio-auric sulphite*, $5K^2SO^3.\overset{'''}{Au}{}^2(SO^3)^3.5H^2O$, or $2(KAu'''O^2.4KHSO^3).H^2O$, is obtained by dropping a solution of potassic sulphite into a slightly alkaline solution of potassic aurate, in yellow needles insoluble in the alkaline liquid, but dissolving in water, with evolution of sulphurous acid and separation of gold. Acids likewise decompose it. When heated, it leaves metallic gold and sulphate of potassium. (Frémy.)

Sodio-aurous sulphite, $2Na^3Au(SO^3)^2.5H^2O$, or $3Na^2SO^3.Au^2SO^3.5H^2O$, forms a colourless solution, which is precipitated by alcohol, appears yellow by reflected light (like fulminating gold), purple by transmitted light (like purple of Cassius). Its solution gives with nitrate of silver a precipitate of the colour of lead-chromate, and forms with lead-salts a red insoluble compound. (Heintz.)

Sulphites of Iridium. (Birnbaum, Ann. Ch. Pharm. cxxxvi. 177; Jahresb. 1865, p. 283.)—*a. Iridic Sulphite,* $IrO^2.SO^2.4H^2O = \left.\begin{matrix}(SO)''\\(IrO)''\end{matrix}\right\}O^2$.—On passing sulphurous oxide into water in which iridic oxide (iii. 322) is suspended, part of the oxide dissolves with light olive-green colour, while the rest remains undissolved as brownish-green iridic sulphite. This salt, when dry, forms a black-brown amorphous mass; which, when heated, gives off water, sulphurous acid and sulphuric acid, and leaves black oxide of iridium. Hydrochloric and sulphuric acids dissolve it with green colour and evolution of sulphurous oxide; nitric acid and potash separate blue iridic oxide.

β. Iridious Sulphite, $\overset{'''}{Ir}{}^2(SO^3)^3.6H^2O = \left.\begin{matrix}(\overset{''}{SO})^3\\(Ir''')^2\end{matrix}\right\}O^6.6H^2O$.—This salt is contained in the light olive-green solution above mentioned, and separates by gradual evaporation as a brown amorphous mass. It dissolves easily and with grey colour in acids, and when heated with potash, becomes first brown, then green and blue.

The following double salts of iridious sulphite are obtained by mixing the olive-green liquid filtered from iridic sulphite with the corresponding alkaline carbonates, in quantity not sufficient to form a precipitate. The solutions, when left to themselves, deposit the double salts as dark crystalline precipitates:

Ammonio-iridious sulphite,	$(NH^4)^3Ir'''(SO^3)^3.3H^2O$.
Potassio-iridious sulphite,	$K^3Ir'''(SO^3)^3.3H^2O$.
Sodio-iridious sulphite,	$Na^3Ir'''(SO^3)^3.4H^2O$.

Respecting other double sulphites of iridium, see vol. iii. p. 322.

Sulphites of Iron.—*a. Ferric salts.*—The *neutral salt,* $Fe^2O^3.3SO^2 = Fe^2(SO^3)^3 = \left.\begin{matrix}(\overset{''}{SO})^3\\(Fe''')^2\end{matrix}\right\}O^6$, is not known in the solid form. The red solution formed by dissolving ferric hydrate in sulphurous acid, or adding an alkaline sulphite to a ferric salt, quickly becomes converted into ferrous sulphate.—The *dibasic salt,* $2Fe^2O^3.3SO^2 = Fe^2O^3.Fe^2(SO^3)^3 = \left.\begin{matrix}(\overset{''}{SO})^3\\(Fe''')^4\end{matrix}\right\}O^9$, is thrown down by alcohol from the red solution above mentioned, as a yellow-brown hydrated precipitate, which oxidises in the air to soluble ferric sulphate.—The *tribasic salt,* $Fe^2O^3.SO^2.6H^2O = 2Fe^2O^3.Fe^2(SO^3)^3.18H^2O = \left.\begin{matrix}(SO)''\\(Fe''')^2\end{matrix}\right\}O^4.6H^2O$, is produced by treating the dibasic salt with water. A solution of ferric oxide in sulphurous acid, exposed to the air for several days, deposits the tribasic salt as a red-brown precipitate containing 7 at. water (Muspratt, Koene). If, on the other hand, the same solution is heated, it deposits a straw-yellow ochry precipitate, which contains, according to Koene, $3Fe^2O^3.SO^2.7H^2O$, and suffers no alteration on exposure to the air.

Potassio-ferric Sulphites.—The blood-red solution obtained by passing sulphurous gas through water in which ferric hydrate is suspended, yields, on addition of caustic potash, a double salt containing $(Fe^2O^3.SO^2).2(K^2O.SO^2).5H^2O = \left.\begin{matrix}(S''O)^3\\(Fe''')^2K^4\end{matrix}\right\}O^8.5H^2O$ (Muspratt).—Another double salt, $(Fe^2O^3.SO^2).K^2O.2SO^2$, is formed, according to Koene, as a deep-yellow precipitate on adding dilute potash-ley to the alcoholic filtrate obtained in the preparation of dibasic ferric sulphite.

β. Ferrous sulphite, $Fe''SO^3.3H^2O$, is obtained, together with an equivalent quantity of the hyposulphite, by dissolving clean iron-wire in aqueous sulphurous acid (Fordos and Gélis). On leaving this solution to evaporate in a vacuum, the sulphite separates out first in pale-green crystals; or it may be precipitated as a white powder by adding alcohol to the solution. It is also produced by dissolving recently precipitated ferrous carbonate in sulphurous acid. The nearly colourless crystals dissolve sparingly in water, but abundantly in aqueous sulphurous acid, and are converted slowly in dry, quickly in moist air, into sulphate. (Muspratt.)

Sulphite of Lead, $Pb''SO^3$, prepared by double decomposition, or by passing sulphurous oxide into a solution of neutral plumbic acetate, is a white, insoluble, anhydrous powder, which when heated gives off sulphurous oxide, and leaves a mixture of sulphate and sulphide. It has been proposed as a substitute for white lead.

Sulphite of Lithium, $Li^2SO^3.6H^2O$, separates from its aqueous solution on boiling, or on addition of alcohol, in white feathery crystals, which turn light-yellow on exposure to the air. (Danson.)

Sulphite of Magnesium, $Mg''SO^3.6H^2O$, forms small shining crystals, belonging to the rhombohedral system, which dissolve in 20 pts. of cold water, and are gradually converted into sulphate on exposure to the air. It gives off part of its water at 100°, the rest, together with sulphurous oxide, at 200° (Rammelsberg).—Muspratt obtained a salt with 3 at. water, crystallising in oblique rhombic prisms.

Ammonio-magnesic sulphite, $(NH^4)^2\overset{''}{Mg}{}^3(SO^3)^4.5H^2O$, is obtained, according to Rammelsberg, by mixing a solution of magnesia in sulphurous acid, with excess of ammonia, dissolving the resulting precipitate in sulphurous acid, and leaving the solution to crystallise. Sulphite of magnesium then separates out first, and afterwards the much more soluble double salt.—Another hydrate, containing $(NH^4)^2\overset{''}{Mg}{}^3(SO^3)^4.18H^2O$, is obtained in monoclinic crystals from the mixed solution of the component salts (Rammelsberg).—The potassic double salt is difficult to obtain pure, because it is about as soluble as the simple magnesic sulphite formed at the same time.

Sulphite of Manganese, $Mn''SO^3.2H^2O$ or (according to Rammelsberg) $2Mn''SO^3.5H^2O$, is a reddish-white crystalline powder, tasteless at first, but leaving a nauseous metallic aftertaste. It is insoluble in water, alcohol, and ether, and permanent in the air (Muspratt, John). When heated in a small retort, it gives off water and sulphurous oxide, and leaves a greenish-brown pulverulent residue of manganic oxide, manganous sulphate, and sulphide of manganese. (Rammelsberg.)

Sulphites of Mercury.—*a. Mercuric salts.*—When a syrupy solution of basic mercuric nitrate is mixed with a dilute solution of alkaline sulphite, a heavy white curdy precipitate is formed, varying in composition between the neutral salt, $Hg''O.SO^2$, or $Hg''SO^3$, and the basic salt, $2Hg''O.SO^2$ or $Hg''O.Hg''SO^3$, according as the mercuric salt used in the preparation contained less or more of base.—The *neutral salt*, $Hg''SO^3$, is very unstable, and is converted by boiling with water into a mixture of mercurous sulphate and metallic mercury.—The *basic salt*, $Hg''O.Hg''SO^3$, when gently heated in the dry state, or boiled with water, is converted, without alteration of percentage composition, into neutral mercurous sulphate, Hg^2SO^4 (Péan-de-St-Gilles, Ann. Ch. Phys. [3], **xxxvi.** 80).—The nitrate is the only mercuric salt from which mercuric sulphite can be prepared, all others being reduced or dissolved by alkaline sulphites.

Acid mercuric sulphite, $Hg''H^2(SO^3)^2$, is formed, according to Wicke, by treating solid mercuric chloride with a solution of acid sulphite of sodium, and separates as a white crystalline powder consisting of microscopic cubes. It is moderately soluble in water. The solution deposits metallic mercury when heated; it is decomposed by potash in the cold, by ammonia only when heated, with formation of a white precipitate; it is not precipitated by alkalis.

Ammonio-mercuric Sulphite, $(NH^4)^2Hg''(SO^3)^2$.—A solution of acid ammonium-sulphite, saturated at the boiling heat with mercuric oxide, and then left to evaporate at a gentle heat, deposits this double salt in large, transparent, colourless, soft, tabular crystals. It decomposes when exposed to light, with separation of mercury-globules; slowly also even when kept in the dark and in well-closed vessels. The aqueous solution decomposes in the same way, slowly in the cold, immediately on boiling. With potash it yields a white precipitate, consisting of $2Hg''SO^3.N^2\overline{Hg}{}^3.2H^2O$. (Hirzel.)

Potassio-mercuric sulphite, $K^2Hg''(SO^3)^2.H^2O$, separates from a mixture of the saturated solutions of potassic sulphite and mercuric chloride, in tufts of small white needles. It dissolves slightly in cold water, forming a neutral solution. (Péan-de-St-Gilles.)

Sodio-mercuric sulphite, $Na^2Hg''(SO^3)^2.H^2O$, is obtained by adding mercuric chloride to excess of sodic sulphite. On evaporating the liquid, the salt crystallises in small rhombohedral plates, whose solution has a neutral reaction, and is not precipitated by iodide of potassium (Péan de St-Gilles).—Another double salt, containing $Na^2Hg^2(SO^3)^3.H^2O$, is produced, with separation of a small quantity of calomel, on mixing the hot saturated solutions of sodic sulphite and mercuric chloride, the latter being in excess. The liquid, filtered hot, deposits the double salt on cooling as a compact mass of indistinct needle-shaped crystals. It is more soluble than the preceding. The solution has an alkaline reaction, and iodide of potassium separates half the mercury from it. Potash heated with it separates one-fourth of the mercury. (Péan-de-St-Gilles.)

A compound of *ammonium-sulphite* with *mercuric chloride*, $2(NH^4)^2SO^3.3Hg''Cl^2$, separates in nacreous crystalline laminæ, on mixing the solutions of the component salts. When heated to boiling with water, it gives off sulphurous oxide, and deposits mercurous chloride.

β. Mercurous Sulphite.—The neutral salt is not known. An *anhydrosulphite*, $2Hg^2O.3SO^2 = 2Hg^2SO^3.SO^2$, or $3Hg^2O.4SO^2 = 3Hg^2SO^3.SO^2$, is produced by passing sulphurous oxide through water in which recently precipitated mercuric oxide is suspended. It is a white, very easily decomposible salt, being quickly oxidised to sulphate, with separation of metallic mercury. When heated in a test-tube, it melts, gives off a large quantity of sulphurous oxide, and yields a sublimate of mercurous sulphite and metallic mercury. It is also quickly decomposed by boiling with water, mercury being separated, and free sulphuric acid remaining in solution. Warm nitric acid dissolves it easily, with evolution of nitrous acid. Hydrochloric acid converts it into mercurous chloride. When it is digested with caustic potash, the filtrate which runs away from the black mercurous oxide, contains but little sulphite of potassium. (Rammelsberg.)

Sulphite of Nickel, $Ni''SO^3.6H^2O$, separates by spontaneous evaporation from its aqueous solution, in fine tetrahedrons. It is insoluble in pure water, soluble in water containing sulphurous acid, and becomes opaque when heated with water, probably in consequence of conversion into the anhydrous salt, or of another hydrate (Muspratt). —The *tetrahydrated salt*, $Ni''SO^3.4H^2O$, is obtained, according to Muspratt, by boiling the solution of nickel-hydrate in sulphurous acid; it then separates in small green crystals, nearly insoluble in water. .Metallic nickel is dissolved by aqueous sulphurous acid, with formation of sulphite and hyposulphite of nickel; on evaporating the solution, the sulphite crystallises out with 6 at. water. (Fordos and Gélis.)

An *ammonio-sulphite of nickel*, $Ni''SO^3.3NH^3.3H^2O$, is thrown down by alcohol from a solution of nickel-sulphite in ammonia, as a light-blue crystalline precipitate, which dissolves in a small quantity of water to a light-blue liquid, becoming turbid when mixed with more water, or when heated. (Rammelsberg.)

Sulphites of Osmium.—*Osmious Sulphite*, $Os''SO^3$, is formed by treating aqueous osmic acid with sulphurous acid, and separates on mixing the solution with sulphate or carbonate of sodium, and leaving it to evaporate, or warming it, as a blue jelly, which, while moist, oxidises readily, with formation of sulphuric acid, but, after drying, forms an almost unalterable powder of a dull black-blue colour. It is insoluble in water, but dissolves easily in hydrochloric acid, forming an indigo-coloured solution without evolution of sulphurous oxide. It is decomposed by potash at the boiling heat, and when heated by itself is resolved into sulphide of osmium, osmic tetroxide, and sulphurous anhydride. (Claus, J. pr. Chem. xc. 65; Jahresb. 1863, p. 295.)

The salt, $OsO.2SO^2.6KCl$, is obtained by treating the following compound with hydrochloric acid: it forms a brown-red crystalline salt, having a sharp taste, and very soluble in water. (Claus, Ann. Ch. Pharm. lxvii. 375.)

Osmio-potassic Sulphite, $Os''H^2(SO^3)^2.3K^2SO^3.4H^2O$, or $Os''K^6H^2(SO^3)^5.4H^2O$, is formed by heating osmio-potassic chloride with a solution of potassic sulphite. It is a light, white, or faintly rose-red powder, consisting of small, soft, crystalline scales. It is very slightly soluble in water, and decomposes at 180°. (Claus, Ann. Ch. Pharm. lxiii. 355.)

Sulphites of Platinum.—*a. Platinic Sulphite*, $Pt^{iv}(SO^3)^2$, obtained by dissolving platinic oxide in sulphurous acid, and gradual evaporation, is a white gummy mass, soluble in water and in alcohol, and having a strong acid reaction. When heated it is resolved into metallic platinum and sulphuric anhydride. From a solution of auric chloride it throws down metallic gold, the solution then containing platinic chloride and sulphuric acid. It is not decomposed by sulphuric or by hydrochloric acid. It forms double salts with sulphites of alkali-metal. (Döbereiner.)

β. Platinous Sulphite, $Pt''SO^3$, is obtained by passing sulphurous oxide through water in which platinous oxide is suspended. On leaving the liquid to itself with the vessel closed airtight, the oxide gradually dissolves, forming a brown-green solution. It forms colourless double salts with sulphites of alkali-metals.

Ammonio-platinous Sulphite, $(NH^4)^2Pt''(SO^3)^2.H^2O$, discovered by Liebig and analysed by Böckmann, is prepared by reducing a solution of platinic chloride to platinous chloride with sulphurous acid, neutralising with ammonia, precipitating with alcohol, and crystallising from water. Forms long, flat, white needles, easily soluble in water. —Another ammonio-platinous sulphite, containing $(NH^4)^6Pt''(SO^1)^4$, is formed, as a white, bulky, crystalline precipitate, on mixing a moderately concentrated solution of ammonio-platinous chloride with neutral sulphite of ammonium. (J. Lang, J. pr. Chem. lxxxiii. 415.)

Potassio-platinous Sulphite, $2K^6Pt''(SO^3)^4.3H^2O$, produced by heating potassio-platinous chloride with acid sulphite of potassium, crystallises in microscopic six-sided prisms, having a faint straw-yellow colour, sparingly soluble in cold, easily in warm water. The neutral solution is decomposed by hydrochloric acid, only when heated; hydrate and carbonate of potassium do not alter it, even with aid of heat; carbonate of sodium throws down a white precipitate of the sodium double salt; carbonate of ammonium and sulphydric acid do not act upon it (Lang). Claus, by decomposing platinic chloride with sulphite of potassium, obtained the salt $K^6Pt''H^2.(SO^3)^5.H^2O$, analogous to the osmium-salt above described. Lang was not able to prepare this salt.

Sodio-platinous Sulphite, $Na^6Pt''(SO^3)^4.3H^2O$, prepared by reducing platinic chloride to platinous chloride with sulphurous acid, saturating the liquid with sulphurous acid. and exactly neutralising with sodic carbonate, is a bulky nearly colourless precipitate, which dries up to a white amorphous powder, acquiring a tinge of yellow when moistened. It is sparingly soluble in cold, more soluble in warm water, insoluble in alcohol. From the aqueous solution it is precipitated unaltered by the chlorides of sodium, ammonium, and barium, and by nitrate of silver. It gives off its water of crystallisation between 180° and 200°, and may then be heated to 240° without alteration; but at higher temperatures it becomes darker, and is completely decomposed at a red heat. The platinum in this salt cannot be detected by the ordinary reagents; but strong acids decompose the salt, eliminating sulphurous oxide, and converting it into the following compound. By cyanide of potassium it is dissolved and converted into potassio-platinous cyanide. (Litton and Schnedermann, Ann. Ch. Pharm. xliii. 316.—Lang.)

Another sodio-platinous sulphite, $Na^2Pt''(SO^2)^2.H^2O$, is obtained by dissolving the preceding in dilute hydrochloric or sulphuric acid, and leaving the solution to evaporate. It is then deposited as a yellow powder, moderately soluble in water, and forming a slightly acid solution, from which it is precipitated by common salt. In other respects it resembles the preceding compound. (Litten and Schnedermann.)

Argento-platinous Sulphite, $Ag^6Pt''(SO^3)^4$, produced by mixing the corresponding potassium-salt with nitrate of silver, is a white precipitate, insoluble in water, easily soluble in ammonia. (Lang.)

Sulphites of Potassium.—The *neutral salt*, $K^2SO^3.2H^2O$, is obtained by saturating a solution of the carbonate with sulphurous acid, and evaporating over oil of vitriol, in large monoclinic octahedrons, somewhat deliquescent, very soluble in water, slightly soluble in alcohol, having a strong alkaline reaction and bitter taste. When heated, it swells up, gives off sulphurous oxide, and leaves sulphate of potassium mixed with sulphide and hydrate. (Muspratt.)

The *acid salt*, $KHSO^3$, is produced by supersaturating a warm and moderately concentrated solution of the carbonate with sulphurous acid, and separates on cooling, or on addition of absolute alcohol, as a white mass of crystalline needles. The solution, if left for several weeks in a stoppered bottle, deposits the salt in large rhombic prisms. It has a disagreeable sulphurous aftertaste, a neutral reaction, gives off sulphurous oxide continually on exposure to the air, and is finally converted into sulphate. Its solution, when evaporated, gives off sulphurous acid, leaving a mixture of acid and neutral salt, and after prolonged boiling, only the neutral salt remains. (Muspratt, Rammelsberg.)

An *anhydrosulphite*, $K^2O.2SO^2$, or $K^2SO^3.SO^2$, is formed by passing sulphurous oxide through a warm concentrated solution of the carbonate, till the effervescence ceases and the liquid assumes a greenish colour. It is then deposited on cooling, in hard granular crystals, which must be collected on a filter, washed with alcohol, and dried between filter-paper. It dissolves very slowly in water, very slightly in alcohol, and not at all in ether, has a disagreeable saline taste, and is permanent in the air. When heated, it gives off sulphurous oxide and sulphur, leaving a residue of potassic sulphate. (Muspratt.)

Sulphite of Rhodium. See RHODIUM (p. 105).

Sulphite of Ruthenium and Potassium, $K^2Ru''(SO^3)^2$, is produced, according to Claus, as a cream-coloured pulverulent precipitate, by boiling potassio-ruthenious chloride with sulphite of potassium. By repeated solution and evaporation it may be obtained nearly white. (Claus.)

Sulphite of Silver, Ag^2SO^3, is prepared by dissolving silver-oxide in sulphurous acid, or by precipitating a silver-salt with an alkaline sulphite or sulphurous acid; and is deposited, according to the mode of preparation, in small white shining needles, or as a white precipitate resembling chloride of silver. The salt is very slightly soluble in water, has a disagreeable taste, and, according to Muspratt, acquires, on exposure to the air, a dark purple and ultimately black colour. According to Fourcroy, the crystals are unalterable even in sunlight. It forms double salts with alkaline sulphites.

Sulphites of Sodium.—The *neutral salt*, Na^2SO^3, is easily prepared by saturating a solution of the carbonate with sulphurous acid, and adding to it, while warm, as much sodic carbonate as it originally contained. The salt then separates on cooling in monoclinic crystals containing $Na^2SO^3.7H^2O$. It is very soluble in water; the solution has an alkaline reaction, and, when heated, deposits a salt (probably anhydrous), which disappears again on cooling. It dissolves slightly in aqueous alcohol. At 150° it gives off the whole of its water, becoming white and enamel-like, and at a higher temperature melts to a yellowish-red mass, from which alcohol extracts sulphide of sodium, leaving sulphate (Rammelsberg).—Another hydrate, containing $Na^2SO^3.10H^2O$, is produced, according to Muspratt, by saturating a solution of sodic carbonate with sulphurous acid till it acquires an acid reaction, and leaving it over oil of vitriol. It then separates in large oblique prisms, which, on exposure to the air, quickly effloresce, and are gradually converted into sulphate. It has a faint alkaline reaction and cooling sulphurous taste (Muspratt). Specific gravity of the decahydrated crystals = 1·561 (Buignet, Jahresb. 1861, p. 15).—Vauquelin obtained the neutral sulphite with 8 at. water.

Acid sulphite, $NaHSO^3$.—A solution of sodic carbonate, supersaturated, while warm, with sulphurous acid, deposits this salt on cooling in small shining prisms. Alcohol precipitates it in the granular form. It smells of sulphurous acid, has an acid reaction, an unpleasant sulphurous taste, effloresces very easily in the air, and is finally converted into sulphate (Muspratt). Clark obtained an acid salt with 9 at. water.

Sodio-ammonic sulphite, $Na^2(NH^4)H(SO^3)^2.8H^2O$, crystallises, according to Marignac, in thin monoclinic tablets.

Sulphite of Strontium, $Sr''SO^3$, is obtained by double decomposition, as a white tasteless powder, and in crystalline grains by dissolving the precipitate in aqueous sulphurous acid, or by passing sulphurous oxide through water in which carbonate of strontium is suspended (Muspratt). The crystals are flat rectangular plates, acuminated with two faces (Rammelsberg). The salt is gradually converted into sulphate by exposure to the air.

Sulphite of Titanium is precipitated, according to Berthier, on boiling a solution of titanic hydrate in sulphurous acid.

Sulphites of Uranium. *Uranic Sulphite*, or *Sulphite of Uranyl*, $Ur^2O^3.SO^2.3H^2O = (Ur^2O^2)''SO^3.3H^2O$, separates as a flocculent precipitate, of a fine light-yellow colour, on mixing the nitrate with sulphite of ammonium, or on passing sulphurous oxide through water in which uranic hydrate is suspended. It is permanent in the air at ordinary temperatures, but decomposes when heated, giving off sulphurous oxide, and leaving a brown residue, probably of uranoso-uranic oxide (Muspratt). According to Reinele (Pogg. Ann. cxxv. 238), a solution of uranic nitrate mixed with sulphite of ammonium yields a lemon-yellow or sulphur-yellow precipitate, consisting of $(U^2O^2)''SO^3.2H^2O$, mixed with variable quantities of uranate of ammonium; it is soluble in excess of ammonium-sulphite, and somewhat soluble even in water. According to Girard (Compt. rend. xxxiv. 22; Jahresb. 1852, p. 376), the salt obtained by passing sulphurous oxide through water in which uranic oxide is suspended, and leaving the solution to evaporate, contains $(U^2O^2)''SO^3.4H^2O$.

Uranous Sulphite.—A basic salt, $Ur''SO^3.Ur''H^2O^2.H^2O$, is precipitated, with evolution of sulphurous oxide, on mixing a solution of uranous chloride with sulphite of sodium. It has a grey-green colour, dissolves easily in acids, and, when heated, gives off sulphurous oxide and leaves uranoso-uranic oxide.

Sulphite of Yttrium, $Y''SO^3$, is a white powder, insoluble in water, slightly soluble in sulphurous acid. Its solution, when evaporated, yields crystals of yttric sulphate. (Berlin, Pogg. Ann. xliii. 105.)

Sulphite of Zinc, $Zn''SO^3.2H^2O$ (according to Fórdos and Gélis), or $2Zn''SO^3.5H^2O$ (according to Rammelsberg), crystallises, on evaporating a solution of zinc-carbonate in sulphurous acid, in small sparingly soluble prisms having an unpleasant astringent taste. It is precipitated from the aqueous solution by alcohol or ether in needle-shaped crystals. On exposure to the air, it is quickly converted into sulphate, and, when heated, gives off water and sulphurous oxide, leaving a residue of sulphate, sulphide, and oxide of zinc.

An *acid sulphite of zinc-ammonium*, $\left.\begin{matrix} NZn''H^3 \\ H \end{matrix}\right\} SO^3$, is obtained in crystalline crusts by dissolving zinc-sulphite in warm aqueous ammonia, and evaporating at a gentle heat. It smells of ammonia, and is decomposed by water, which dissolves out sulphite of ammonium. (Rammelsberg.)

Sulphite of Zirconium is a white powder, insoluble in water, somewhat soluble in sulphurous acid, and precipitated from the solution by boiling. (Berthier.)

Alcoholic Sulphites. Sulphurous Ethers.

The two atoms of hydrogen in the molecule of sulphurous acid, $\left.\begin{matrix}(SO)''\\H^2\end{matrix}\right\}O^2$, may be partly or wholly replaced by monatomic alcohol-radicles, giving rise to acid and neutral sulphurous ethers, represented by the general formulæ:

$$\underset{\text{Acid.}}{\left.\begin{matrix}(SO)''\\R.H\end{matrix}\right\}O^2} \text{ and } \underset{\text{Neutral.}}{\left.\begin{matrix}(SO)''\\R^2\end{matrix}\right\}O^2}.$$

The acid ethers may also be regarded as compounds of sulphuric anhydride with hydrocarbons containing even numbers of hydrogen-atoms, and are sometimes designated as sulpho-acids, *e.g.*:

$$\text{Phenylsulphurous acid, } \left.\begin{matrix}(SO)''\\C^6H^5.H\end{matrix}\right\}O^2 \quad = \quad C^6H^6.SO^3, \quad \text{Sulphobenzolic acid.}$$

No neutral sulphurous ethers are at present known of the form $\left.\begin{matrix}(SO)''\\R''\end{matrix}\right\}O^2$, but there is a group of acid ethers, $\left.\begin{matrix}(SO)^2\\R''H^2\end{matrix}\right\}O^4$, derived from a double molecule of sulphurous acid, $H^4S^2O^6$, by substitution of a diatomic alcohol-radicle for half the hydrogen. These are the so-called disulpho-acids, which may also be formulated as compounds of hydrocarbon with 2 at. SO^3, *e.g.*:

$$\text{Phenylene-sulphurous acid, } \left.\begin{matrix}(SO)^2\\(C^6H^4)''\\H^2\end{matrix}\right\}O^4 \quad = \quad C^6H^6.2SO^3, \quad \text{Disulphobenzolic acid.}$$

The acid sulphurous ethers of the monatomic alcohol-radicles, C^nH^{2n+1}, homologous with ethyl, are produced by the action of oxidising agents, especially of nitric acid, on the sulphides, sulphydrates, and sulphocyanates of the corresponding radicles; methylsulphurous acid also, by electrolytic reduction of its chlorinated derivatives (p. 555); these ethers do not appear to be formed by the action of sulphurous acid on the corresponding alcohols.

The acid sulphurous ethers of other alcohol-radicles (phenyl, naphthyl, &c.) are produced by the action of strong sulphuric acid on the corresponding hydrocarbons containing even numbers of hydrogen-atoms, *e.g.*:

$$\underset{\text{Benzene.}}{C^6H^6} + H^2SO^4 = H^2O + \underset{\text{Phenylsulphurous acid.}}{(C^6H^5)HSO^3}.$$

All these ethers are monobasic acids, forming well-defined crystalline salts. The potassium-salts of phenylsulphurous and benzylsulphurous acid are decomposed by fusion with excess of *potassic hydrate*, yielding sulphate of potassium and the corresponding alcohols, phenol and cresol, *e.g.*:

$$\underset{\text{Benzylsulphite of potassium.}}{(C^7H^7)KSO^3} + KHO = K^2SO^3 + \underset{\text{Cresol.}}{(C^7H^7)HO}.$$

The salts of all the acid sulphurous ethers are converted by pentachloride of phosphorus into chlorides derived from the acid ethers by substitution of chlorine for hydroxyl, *e.g.*:

Ethylsulphurous acid . . . . . $SO.C^2H^5O.HO$.
Ethylsulphurous chloride . . . . . $SO.C^2H^5O.Cl$.

These chlorine-compounds, when enclosed in sealed tubes, gradually resolve themselves into a chloride of the alcohol-radicle, RCl, and sulphurous oxide, SO^2; when heated with pentachloride of phosphorus, they are decomposed according to the general equation:

$$RClSO^2 + PCl^5 = SOCl^2 + RCl + POCl^3.$$

They are converted by caustic potash into the original acid ethers; by ammonia into amides; by alcohols into the corresponding neutral ethers, *e.g.*:

$$\underset{\text{Ethylsulphurous chloride.}}{C^2H^5ClSO} + (C^2H^5)HO = HCl + \underset{\text{Ethylic sulphite.}}{(C^2H^5)^2SO^3};$$

and

$$\underset{\text{Ethylsulphurous chloride.}}{C^2H^5ClSO^2} + (CH^3)HO = HCl + \underset{\text{Methylethylic sulphite.}}{(CH^3)(C^2H^5)SO^3}.$$

The **neutral sulphurous ethers** of the alcohol-radicles C^nH^{2n+1} are also produced by the action of alcohols on disulphide of chlorine (see page 535), or on sulphurous chloride; in the latter case, according to the general equation:

$$SOCl^2 + 2(C^nH^{2n+1})HO = 2HCl + (C^nH^{2n+1})^2SO^3.$$

These neutral ethers are resolved by caustic alkalis into the corresponding alcohols and a sulphite of alkali-metal, *e.g.*:

$$(C^2H^5)^2SO^3 + 2KHO = 2(C^2H^5)HO + K^2SO^3.$$

But the neutral sulphurous ethers of other alcohol-radicles (phenyl, naphthyl, &c.) exhibit a different reaction with alkalis; ethylic naphthylsulphite for example, when treated with potash, yields, not sulphite, but naphthylsulphite of potassium. (**Carius**, Ann. Ch. Pharm. cxiv. 140; Jahresb. 1860, p. 421.)

The **acid sulphurous ethers of diatomic alcohol-radicles**—the so-called **disulpho-acids**, are obtained in some cases by the action of strong sulphuric acid upon hydrocarbons: thus, naphthylene-sulphurous or disulphonaphthalic acid, $C^{10}H^8S^2O^6$, is produced in small quantity, together with naphthylsulphurous acid, by the action of sulphuric acid on naphthalene. More frequently, however, they are produced by the action of fuming sulphuric acid on the cyanides of the alcohol-radicles (nitriles), (or on the corresponding amides, which differ therefrom by addition of 1 at. H^2O): thus phenylic cyanide or benzonitrile, treated with fuming sulphuric acid, yields phenylenesulphurous or disulphobenzolic acid:

$$C^7H^5N + 3H^2SO^4 = C^6H^6S^2O^6 + (NH^4)HSO^4 + CO^2.$$

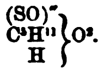
The formation of ethylene-sulphurous acid, and its homologues, may be represented by the general equation:

$$C^nH^{2n+1}.CN + 3H^2SO^4 = (C^nH^{2n})H^2S^2O^6 + (NH^4)HSO^4 + CO^2.$$

They are also produced by the oxidation of the sulphocarbonates of diatomic alcohol-radicles; *e.g.*, ethylene-sulphurous acid, $(C^2H^4)H^2S^2O^6$, by the action of nitric acid on ethylenic disulphocarbonate or trisulphocarbonate (p. 502).

These ethers are dibasic acids, forming acid and neutral salts.

a. Sulphurous Ethers containing Monatomic Alcohol-radicles.



Amylsulphurous Acid, $C^5H^{12}SO^3 = (C^5H^{11})HSO^3 = \left.\begin{matrix}(SO)''\\C^5H^{11}\\H\end{matrix}\right\}O^2$. (**Gerathewohl**, J. pr. Chem. xxxiv. 447.—**O. Henry**, Jun., Ann. Ch. Phys. [3], xxv. 246.—**Medlock**, Ann. Ch. Pharm. lxix. 225.)—This acid is produced by the action of nitric acid on the sulphydrate, disulphide, and sulphocyanate of amyl. When amyl-mercaptan is added by small portions to gently heated nitric acid of specific gravity 1·25, two layers of liquid are obtained, the upper of which is oily, and of variable composition—the lower watery, and consisting of amylsulphurous acid mixed with nitric acid; and on evaporating the latter over the water-bath till the odour of nitrous acid is no longer perceptible, a thick colourless syrup is left, consisting of impure amylsulphurous acid. This product may be used to prepare most of the amylsulphites, inasmuch as on treating the resulting salts with boiling alcohol, the amylsulphite dissolves, while the small quantity of sulphate with which it is mixed remains behind.

The pure acid is obtained by decomposing the lead-salt with sulphuretted hydrogen, and evaporating the filtrate, as a very acid syrup, having a peculiar odour. According to Gerathewohl, it does not crystallise even in a vacuum over oil of vitriol. Medlock, however, obtained it as a deliquescent crystalline mass.

The *amylsulphites* of *ammonium*, *potassium*, and *calcium*, crystallise in colourless laminæ, insoluble in water and in alcohol.—The *barium-salt*, $C^{10}H^{22}Ba''S^2O^6$, forms transparent unctuous scales, which gyrate upon water like amylsulphate or butyrate of barium. It burns in rather strong heat without decomposing.—The *copper-salt* forms bluish-green tables; the *lead-salt*, $C^{10}H^{22}Pb''S^2O^6$, colourless laminæ containing water of crystallisation, which they give off at 120°.—The *silver-salt*, $C^5H^{11}AgSO^3$, crystallises from a moderately concentrated solution in very fine colourless rhombic plates.

DIAMYLIC OR NEUTRAL AMYLIC SULPHITE, $(C^5H^{11})^2SO^3$. (**Carius**, Ann. Ch. Pharm. cvi. 291; cxi. 97; Jahresb. 1858, p. 26; 1859, p. 88.)—Produced by the action of disulphide of chlorine or sulphurous chloride, $(SOCl^2)$, on amylic alcohol, the decomposition in both cases being similar to that which takes place in the preparation of ethylic sulphite (p. 554). The second process is the easier of the two; 1 at. sulphurous chloride being added to 2 at. amylic alcohol, and the resulting liquid freed from hydrochloric acid by passing a stream of carbonic dioxide through it.

Amylic sulphite thus prepared is a nearly colourless oily liquid, smelling like amylic alcohol and ethylic sulphite, giving off sulphurous acid on exposure to moist air, and acquiring a red or brown colour. It is decomposed by water, and more quickly by aqueous alkalis, into amylsulphurous acid and amylic alcohol. When heated above 150° in contact with the air, it begins to decompose into amylic alcohol and sulphurous oxide; but in an indifferent gas, it may, for the most part, be distilled without decomposition at 230°—250.

Benzylsulphurous Acid,* $C^7H^8SO^3 = \left.\begin{matrix}(SO)''\\ C^7H^7\\ H\end{matrix}\right\}O^2$. *Toluenylsulphurous, Sulphotoluic, Sulphotoluenic, Sulphibenzylic,* or *Sulphobenzoenic Acid.* (H. Deville, Ann. Ch. Phys. [3], iii. 172.)—Produced by the action of fuming sulphuric acid on toluene (benzylic hydride, i. 573),† and purified by conversion into a lead-salt, separation by sulphydric acid, and concentration in a vacuum. It crystallises in small very deliquescent laminæ.

Benzylsulphite of ammonium crystallises in small stars; the *potassium-salt* in very soluble anhydrous laminæ; the *barium-salt*, $C^{14}H^{14}Ba''S^2O^6$, in crystalline scales very soluble in water, but not deliquescent.—The *lead-salt* is very soluble.

The benzylsulphites do not precipitate argentic or cupric nitrate.

Cumenylsulphurous Acid, $C^9H^{12}SO^3 = \left.\begin{matrix}(SO)''\\ C^9H^{11}\\ H\end{matrix}\right\}O^2$. *Sulphocumenic Acid.* (Gerhardt and Cahours, Ann. Ch. Phys. [3], i. 87.)—Prepared by adding about 1 pt. of cumene to 2 pts. fuming sulphuric acid, and agitating till the whole is dissolved.—The *barium-salt*, $C^{18}H^{24}Ba''S^2O^6$, obtained by saturating the acid solution with carbonate of barium, crystallises in a mass of nacreous very brilliant laminæ, resembling fish-scales. Its solution is not decomposed by boiling, and does not precipitate the solution of calcic chloride, plumbic acetate, mercuric chloride, cupric chloride, nickel-chloride, or bismuth-chloride.

Ethylsulphurous Ethers.—Three of these compounds are known: viz., ethylsulphurous acid, produced by the action of oxidising agents on sulphydrate and sulphocyanate of ethyl;—ethylsulphurous chloride, by the action of phosphoric oxychloride on metallic ethylsulphites;—and neutral ethylic sulphite, by the action of alcohol on disulphide of chlorine, sulphurous chloride, or ethylsulphurous chloride.

ETHYLSULPHUROUS ACID, $C^2H^6SO^3 = (C^2H^5)HSO^3$. *Sulphetholic Acid. Hyposulphethylic Acid.* (Löwig and Weidmann, Pogg. Ann. xlvii. 153; xlix. 329.—Kopp, Ann. Ch. Pharm. xxxv. 346.—Muspratt, Chem. Soc. Qu. J. iii. 18; Compt. Chim. 1848, p. 10.)—This acid is produced:—1. By the prolonged action of nitric acid (specific gravity = 1·23) on mercaptan. The resulting liquid is evaporated, diluted with water, neutralised with carbonate of lead, filtered, and concentrated; the lead-salt, after crystallisation, is decomposed by sulphydric acid; and the filtrate concentrated by evaporation.—2. By the action of moderately dilute nitric acid on ethylic sulphocyanate. The liquid is cohobated five or six times, then evaporated to a syrup, which after dilution is saturated with carbonate of barium; and the barium-salt thus obtained is decomposed by sulphuric acid. In both modes of preparation sulphuric acid is formed as well as ethylsulphurous acid, and in greater quantity as the nitric acid is more concentrated.—3. By treating ethylic sulphocyanate with a mixture of hydrochloric acid and potassic chlorate.

Ethylsulphurous acid concentrated by evaporation forms a heavy oil, of specific gravity 1·30, in which limpid crystals gradually form, especially at low temperatures. It has no smell, but a very sour taste, with disagreeable aftertaste, like that of phosphoretted hydrogen. It dissolves in all proportions in *water* and in *alcohol*, and absorbs moisture from the air. It bears a rather high temperature without decomposition, but if very strongly heated, gives off sulphuric acid and sulphurous anhydride. Fused with *hydrate of potassium*, it yields a product from which hydrochloric or sulphuric acid eliminates a large quantity of sulphurous acid.

The ethylsulphites, $C^2H^5MSO^3$, are soluble in water and in alcohol, and have a disagreeable taste, like that of the acid. They decompose when strongly heated, turning black, giving off sulphurous anhydride, together with fetid sulphurous vapours, which burn with a violent flame, and leaving a carbonaceous residue containing metallic sulphide and sulphate.—The *ammonium-salt* crystallises in very deliquescent tablets.—The *potassium-salt*, $C^2H^5KSO^3$ (at 120°) forms lamellar, opaque, deliquescent crystals, sparingly soluble in cold, more soluble in boiling alcohol. It gives off 6·75 per cent. water at 120°, and decomposes at a higher temperature.—The *sodium-salt*,

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* The term benzylsulphurous acid is applied by Kolbe to the compound $C^6H^6SO^3$, more properly called phenylsulphurous or sulphophenylic hydride (p. 562).

† There is formed, at the same time, a crystalline substance, probably homologous with sulphobenzide.

$C^2H^5NaSO^3.xH^2O$, forms deliquescent crystals, exhibiting similar characters.—The *barium-salt*, $C^4H^{10}Ba''S^2O^6.H^2O$, is extremely soluble, but may be obtained in fine rhomboïdal prisms by slow evaporation of a very concentrated solution. It gives off its water at 100°, dissolves very easily in hydrated alcohol, but is insoluble in absolute alcohol, which precipitates it from a strong aqueous solution in silky needles.—The *calcium-salt*, $C^4H^{10}Ca''S^2O^6$ (at 100°), forms limpid crystals resembling the barium-salt, very soluble in water and in alcohol.—The *magnesium-salt* crystallises by cooling in hydrated prisms.—The *cupric salt*, $C^4H^{10}Cu''S^2O^6.5H^2O$, forms light-blue prisms, becoming anhydrous at 120°.—The *ferrous salt*, formed by dissolving metallic iron in a boiling concentrated solution of the acid, crystallises on cooling in colourless prisms. —The *manganese-salt* forms colourless needles.—The *lead-salt*, $C^4H^{10}Pb''S^2O^6$ (at 100°), crystallises from a hot concentrated solution in fine colourless plates.—The *silver-salt*, obtained by saturating the boiling aqueous acid with carbonate of silver, forms colourless laminæ.—The *zinc-salt* forms colourless dendritic crystals, efflorescing in dry air, but absorbing moisture in damp air. The crystallised salt melts when heated, and solidifies in a crystalline mass on cooling. It gives off 8·72 per cent. (2 at.) water at 120°, and 22·96 per cent. (3 at.) more at 180°.

Ethylsulphurous Chloride, $C^2H^5ClSO^2$. (Gerhardt and Chancel, Compt. rend. xxxv. 691.)—This compound, derived from ethylsulphurous acid by substitution of Cl for HO, is easily obtained by distilling ethylsulphite of sodium with excess of phosphoric oxychloride. It is a colourless, slightly fuming liquid, insoluble in *water*, very soluble in *alcohol*, having a specific gravity of 1·357 at 22·5°, and boiling at 171°. Caustic *potash* converts it into a mixture of potassic chloride and ethylsulphite (Gerhardt and Chancel).—When kept in a sealed tube, it is gradually resolved into ethylic chloride and sulphurous anhydride. Heated with *pentachloride of phosphorus* to 120° in a sealed tube, it yields sulphurous chloride, ethylic chloride, and phosphoric oxychloride:

$$C^2H^5ClSO^2 + PCl^5 = SOCl^2 + C^2H^5Cl + POCl^3.$$

Alcohol converts it into neutral ethylic sulphite. (Carius.)

Diethylic Sulphite, $(C^2H^5)^2SO^3$. *Neutral Ethylic Sulphite. Sulphurous Ether.* (Ebelmen and Bouquet, Ann. Ch. Phys. [3], xvii. 66.—Carius, Ann. Ch. Pharm. cvi. 291; cxi. 93; Jahresb. 1858, p. 94; 1859, p. 87.)—This ether is produced:—1. By the action of absolute alcohol on disulphide of chlorine. According to Carius, the first products are sulphurous chloride and ethylic sulphydrate:

$$S^2Cl^2 + C^2H^6O = SOCl^2 + C^2H^6S;$$

and these, by their mutual action, produce ethylic sulphite, together with ethylic chloride, hydrochloric acid, and free sulphur:

$$3SOCl^2 + 4(C^2H^5)HS = (C^2H^5)^2SO^3 + 2C^2H^5Cl + 4HCl + S^6.$$

The alcohol is to be added in excess to the sulphide of chlorine (Carius); the liquid filtered from the precipitated sulphur is distilled; and the portion which goes over, between 150° and 170°, is collected apart. (Ebelman and Bouquet.)

2. By the action of sulphurous chloride on alcohol:

$$SOCl^2 + 2(C^2H^5)HO = 2HCl + (C^2H^5)^2SO^3.$$

The alcohol must be perfectly anhydrous, and added by drops to the sulphurous chloride; but the result is not affected by the proportions in which the two substances are ultimately mixed. (Carius.)

3. By the action of absolute alcohol on ethylsulphurous chloride (Carius):

$$C^2H^5ClSO^2 + (C^2H^5)HO = HCl + (C^2H^5)^2SO^3.$$

Ethylic sulphite is a limpid colourless liquid, having an odour somewhat like that of mint. Boiling-point 160°. Specific gravity of liquid = 1·085 at 16°; of vapour = 4·78. It dissolves in all proportions in *alcohol* and *ether*; *water* precipitates it from the solutions, and gradually decomposes it.—*Chlorine* attacks it strongly, and in bright sunshine forms crystals of trichloride of carbon, C^2Cl^6, together with a strongly fuming liquid containing trichloracetic chloride and chloride of sulphuryl (Ebelmen and Bouquet).—By aqueous *alkalis* or *alkaline carbonates*, it is quickly decomposed into alcohol and an alkaline sulphite. On adding to a dilute solution of the ether in anhydrous alcohol, a quantity of a solution of *potassic hydrate* in absolute alcohol, not sufficient to decompose it completely, a precipitate is formed, consisting of potassic ethylsulphite. When its alcoholic solution is saturated with dry *ammonia-gas*, and heated to 120—140° in a sealed tube, laminar crystals of neutral ammonium-sulphite separate on slow cooling, and the liquid separated therefrom contains ethylamine:

$$(C^2H^5)^2SO^3 + 4NH^3 = (NH^4)^2SO^3 + 2(C^2H^5)H^2N.$$

If the alcoholic solution be saturated with *ethylamine* instead of ammonia, the products are diethylamine and sulphite of ethylamine (Carius).—*Ethylic sulphite* is strongly attached by *pentachloride of phosphorus*, yielding sulphurous chloride, phosphoric oxychloride, and ethylic chloride (Carius):

$$(C^2H^5)^2SO^3 + 2PCl^5 = SOCl^2 + 2C^2H^5Cl + 2POCl^3.$$

ETHYLAMYLIC SULPHITE, $C^7H^{16}SO^3 = \left.\begin{matrix}C^2H^5\\C^5H^{11}\end{matrix}\right\}SO^3$. (Carius, *loc. cit.*)—Produced by the action of ethylsulphurous chloride on amylate of sodium:

$$C^2H^5ClSO^2 + C^5H^{11}NaO = NaCl + (C^2H^5)(C^5H^{11})SO^3.$$

Ethylsulphurous chloride is added to amylic alcohol containing an equivalent quantity of sodium in solution, and the liquid separated from the precipitated chloride of sodium is freed from excess of amylic alcohol by passing a stream of carbonic dioxide through it.

The compound may also be formed by heating ethylsulphurous chloride with amylic alcohol in a sealed tube to 120°; but the hydrochloric acid formed in the reaction acts on another portion of the amylic alcohol, and the water thereby produced decomposes the greater part of the double ether.

Ethylamylic sulphite is a faintly yellowish oily liquid, boiling with partial decomposition between 210° and 225°, and resembling amylic sulphite in all its reactions.

Methylsulphurous Ethers.—There are three compounds of this group, corresponding exactly to the ethylsulphurous ethers: viz., methylsulphurous acid, methylsulphurous chloride, and neutral methylic sulphite; also a methylethylic sulphite.

METHYLSULPHUROUS ACID, $CH^4SO^3 = (CH^3)HSO^3$. *Sulphometholic*, *Methyldithionic*, or *Sulphomethylsulphuric Acid*. (Kolbe, Ann. Ch. Pharm. liv. 174.—Muspratt, *ibid.* lxv. 751; Chem. Soc. Qu. J. iii. 22.)—This acid, discovered by Kolbe in 1845, together with its three chlorinated derivatives, CH^3ClSO^3, $CH^2Cl^2SO^3$, and $CHCl^3SO^3$, is produced: 1. By the electrolytic reduction of either of these chlorinated acids; 2. By the action of nitric acid on sulphocyanate or disulphide of methyl, the operation being conducted in the same manner as for the preparation of ethylsulphurous acid (p. 553). (Muspratt.)

Preparation from Trichloromethylsulphurous Acid.—1. A perfectly neutral solution of potassic trichloromethylsulphite (p. 558), is decomposed by the current of a two-pair Bunsen's battery, the electrodes being formed of amalgamated zinc. The reduction takes place at first with great rise of temperature, but quietly, no hydrogen being evolved at the negative pole till nearly the whole of the trichloromethylsulphite is converted into methylsulphite. After an hour's action of the battery, the liquid becomes so much charged with chloride of zinc, that zinc is deposited at the negative pole. The zinc is then precipitated by carbonate of potassium at the boiling heat; the filtrate evaporated to its former bulk, and the current again made to act upon it, till the quantity of carbonate of zinc (resulting from precipitation of the chloride of zinc, as it forms, by the excess of potassic carbonate) increases to such an amount, that zinc is reduced at the negative pole. The solution is then again precipitated by carbonate of potassium, and the process repeated. The evolution of hydrogen at the negative pole does not begin till 64 pts. of zinc (to 100 pts. of CCl^3KSO^3) have been dissolved at the positive pole. The liquid, in addition to methylsulphite, contains chloromethylsulphite, and a very large quantity of chloride of potassium. It must, therefore, be evaporated to dryness; the residue boiled with alcohol of 80 per cent., filtered from the chloride of potassium, which for the most part remains undissolved; the alcohol distilled off; and the residue, after being diluted with water and mixed with carbonate of potassium, again subjected to the action of the current till the evolution of hydrogen becomes very brisk. This galvanic decomposition (for 70 grammes of trichloromethylsulphite) occupies altogether about ten hours.—2. An amalgam of 1 pt. potassium and 100 pts. mercury is immersed in the aqueous solution of potassic trichloromethylsulphite. Great heat is then evolved, and methylsulphite of potassium is formed, together with hydrate and chloride:

$$CCl^3KSO^3 + 3H^2O + K^6 = CH^3KSO^3 + 3KCl + 3KHO.$$

No hydrogen is evolved till the transformation is complete.

Methylsulphurous acid is extracted from its potassium-salt in the same manner as the corresponding chlorinated acids (p. 557). It forms a thick inodorous liquid, which bears without decomposition a temperature above 300°. It is a strong acid, and forms well-defined salts.

The methylsulphites are soluble in water, and crystallisable; they are decomposed by calcination into metallic sulphide, charcoal, carbonic oxide, and fetid gaseous products containing sulphur.

The *ammonium-salt* forms long deliquescent prisms.—The *potassium-salt*, CH^3KSO^3 (at 100°), crystallises from solution in boiling alcohol of 90 per cent., in a thick pulp of interlaced needles. It becomes moist in the air, but does not deliquesce; its aqueous solution is neutral to test-papers.—An *acid salt*, $CH^3KSO^3.CH^4SO^3$ (at 100°), is obtained by leaving a solution of the neutral salt in methylsulphurous acid to evaporate in a vacuum over oil of vitriol. It forms deliquescent quadrilateral prisms, which strongly redden litmus.

The *barium-salt*, $C^2H^6Ba''S^2O^6$ (at 100°), forms rhombic transparent tablets, permanent in the air; it is precipitated from its aqueous solution by alcohol in shining slender needles.—The *cupric salt*, $C^2H^6Cu''S^2O^6.5H^2O$, forms beautiful very soluble crystals.—The *lead-salt*, $C^2H^6Pb''S^2O^6.H^2O$, obtained by neutralising methylsulphurous acid with carbonate of lead, crystallises in large rhomboïdal prisms, which are permanent in the air, and give off their water of crystallisation at 100°.—A *basic lead-salt*, $C^2H^6Pb''S^2O^6.2Pb''O$ (at 100°), is obtained by boiling the neutral salt with oxide of lead, and evaporating in a vacuum, as a white amorphous mass, the solution of which is precipitated by carbonic acid.

The *silver-salt*, CH^3AgSO^3, crystallises readily in thin anhydrous laminæ, having an acid reaction and sweetish taste, and not very easily altered by exposure to light; the solution may be evaporated by heat without decomposition.

METHYLSULPHUROUS CHLORIDE, CH^3ClSO^2. (Carius, Ann. Ch. Pharm. cxiv. 140; Jahresb. 1860, p. 422.)—Prepared by heating methylsulphurous acid with twice its weight of phosphoric pentachloride, adding a little more of the latter, and isolating by fractional distillation the portion of the product which boils between 150° and 153°. When freshly prepared it is a colourless liquid, having an odour like that of neutral ethylic sulphite, but likewise sharp, and exciting sneezing. It fumes slightly in the air, sinks in water, and is slowly decomposed thereby, yielding hydrochloric and methylsulphurous acid.

DIMETHYLIC or NEUTRAL METHYLIC SULPHITE, $(CH^3)^2SO^3$. (Carius, Ann. Ch. Pharm. cx. 209; cxi. 93; Jahresb. 1859, p. 86.)—Produced by the action of methylic alcohol on disulphide of chlorine or on sulphurous chloride, also by that of methylic alcohol on methylsulphurous chloride, the reactions being exactly similar to those by which ethylic sulphite is obtained (p. 554).

It is a colourless liquid, boiling at 121·5°, under a barometric pressure of 755·4 mm. Specific gravity of liquid = 1·0456 at 16·2° (compared with that of water at 4° as unity): of vapour, obs. = 3·655 to 3·703; calc. = 3·796. When not decomposed by exposure to moist air, it has an agreeable odour resembling that of ethylic sulphate.

It dissolves in all proportions in alcohol and ether; slightly in water, with evolution of sulphurous oxide and formation of methylic alcohol; and reacts with alkalis, ammonia, and pentachloride of phosphorus, exactly like ethylic sulphite.

METHYLETHYLIC SULPHITE, $C^3H^8SO^3 = (CH^3)(C^2H^5)SO^3$. (Carius, Ann. Ch. Pharm. cxi. 93; Jahresb. 1859, p. 88.)—Produced by the action of ethylsulphurous chloride on methylate of sodium, the mode of preparation being similar to that of ethylamylic sulphite (p. 554). It is a colourless fragrant liquid, which, on exposure to the air, takes up water and gives off sulphurous acid. Boiling-point 140° to 141·5°. Specific gravity of the liquid = 1·0675 at 18° (water at 4° = 1); of the vapour = 4·3045. Its reactions are similar to those of ethylic and methylic sulphite.

Chlorinated Methylsulphurous Acids.

Three chlorinated acids are known, derived from methylsulphurous acid by the substitution of one, two, and three atoms of chlorine for hydrogen.

CHLOROMETHYLSULPHUROUS ACID, $CH^3ClSO^3 = (CH^2Cl)HSO^3$. *Chloromethyldithionic Acid, Chlorelayl-hyposulphuric Acid.* (Kolbe, Ann. Ch. Pharm. liv. 174.)—Produced by the partial dechlorination of dichloromethylsulphurous acid, by means of the electric current. To prepare it, the aqueous solution of potassic dichloromethylsulphite, $CHKClSO^3$ (p. 557), is mixed with sulphuric acid, and digested with zinc till saturated therewith. The solution is then left to cool, and decanted from the crystallised zincate of potassium; the rest of the zinc is thrown down from it by boiling with carbonate of potassium; the filtrate is evaporated; and the residue pounded and boiled with alcohol of 80 per cent. On evaporation, chloromethylsulphite of potassium is obtained, mixed however with a considerable quantity of unaltered dichloromethylsulphite. It must therefore be again treated, as above, with sulphuric acid and zinc; and on subsequent treatment with alcohol, but little of the latter salt will remain. To convert this portion likewise, the aqueous solution of the residue, acidulated with a small quantity of sulphuric acid, is exposed to the action of two elements of Bunsen's zinc-carbon battery—the current being conducted into the solution by two amalgamated zinc-plates—till the evolution of hydrogen at the negative pole ceases, and zinc is deposited upon it. The zinc is then precipitated from the solution by carbonate of potassium; the filtrate acidulated with sulphuric acid and again exposed to the electric current; the solution again precipitated with carbonate of potassium; and these operations repeated three or four times, till the whole of the salt is converted into $CClH^2KSO^3$—that is to say, till the salt, when ignited, no longer gives off hydrochloric acid, inasmuch as this acid is evolved from the dichlorinated but not from the monochlorinated salt. To ascertain whether the conversion is complete, a sample of the solution is evaporated to dryness, and exhausted by boiling with absolute alcohol; the crystals, which separate from the alcoholic solution on cooling, are dried and heated in a test-tube; and the condensed drops are mixed with solution of silver. There is no method of separating the two salts. The liquid subjected to the action of the current must always contain free sulphuric acid; otherwise the chloromethylsulphite will be further converted into methylsulphite. As soon as the dichloromethylsulphite has completely disappeared, the liquid is treated with carbonate of potassium to precipitate the zinc; the filtrate evaporated to dryness; the residual mass boiled with alcohol of 80 per cent., which leaves behind the sulphate, and the greater part of the chloride of potassium; the potassium is precipitated from the alcoholic filtrate by sulphuric acid in slight excess; the filtrate evaporated till the boiling-point rises to 130°, and all the hydrochloric acid is expelled; the viscid residue diluted with water; the solution saturated with carbonate of lead, and filtered from the insoluble sulphate of lead; and the filtrate, freed from lead by sulphuretted hydrogen, is again filtered, and concentrated by evaporation. The residue is the concentrated aqueous acid, CH^3ClSO^3.

Chloromethylsulphurous acid is a thickish liquid, syrupy at 16°; strongly acid; yields no crystals; sustains a heat of 140° without decomposition.

The chloromethylsulphites are all soluble in water, and most of them are crystallisable.—The *ammonium-salt* crystallises, by slow evaporation, in deliquescent prisms.—The *potassium-salt*, CH^2KClSO^3, crystallises in needles from a hot saturated solution in alcohol of 96 per cent., the liquid thereby becoming semi-solid. The needles pressed between paper, and dried at 100°, are anhydrous; at a red heat, they give off water and sulphurous oxide, with a trace of sulphur, and leave chloride of potassium much blackened by charcoal:

$$CH^2KClSO^3 = KCl + C + H^2O + SO^2.$$

The salt becomes moist in the air, but does not deliquesce. It does not dissolve in absolute alcohol.

The *sodium-salt* crystallises from boiling alcohol of 96 per cent., in needles united in stellate groups, and deliquescent in the air.—The *barium-salt* forms small rhombic tables, which redden litmus faintly, and have a cooling saline taste.

Lead-salt, $C^2H^4Pb''Cl^2S^2O^6$ (at 100°).—The aqueous acid, saturated with carbonate of lead, and evaporated over oil of vitriol, yields delicate silky needles, united in tufts. After being pressed between paper and dried over oil of vitriol, they appear dull and opaque, and retain 3·7 per cent. (1 at.) water, which escapes at 100°.—The salt dissolves very readily in water, forming a solution which reddens litmus, and tastes sweet at first, but afterwards astringent.

The solution boiled with lead-oxide yields an alkaline filtrate, which deposits carbonate of lead on exposure to the air.

Silver-salt.—The saturated solution of carbonate of silver in the aqueous acid, evaporated over oil of vitriol *in vacuo* and in the dark, leaves a pale-yellow viscid liquid, which with difficulty yields small crystals, having a slight acid reaction, a sweetish and disagreeably metallic taste, and very sensitive to light and heat.

DICHLOROMETHYLSULPHUROUS ACID, $CH^2Cl^2SO^3 = (CHCl^2)HSO^3$. *Dichloromethyldithionic* or *Chloroformyl-hyposulphurous Acid.* (Kolbe, *loc. cit.*)—This acid is obtained:—1. As a zinc-salt, by dissolving zinc in trichloromethylsulphurous acid:

$$2CHCl^3SO^3 + Zn^2 = C^2H^2Cl^4Zn''S^2O^6 + Zn''Cl^2.$$

The zinc is precipitated from the resulting solution by carbonate of potassium; the filtrate evaporated to dryness; and the residue is boiled with alcohol of 96 per cent.: the solution, as it cools, deposits crystals of potassic dichloromethylsulphite.

2. More easily, as a potassium-salt, by boiling dichloromethylsulphurous chloride, $CHCl^3SO^2$ (p. 559), with potash:

$$CHCl\,SO^2 + KHO = CHCl^2KSO^3 + HCl.$$

The excess of potash is neutralised with carbonic acid; the liquid evaporated to dryness; and the dichloromethylsulphite of potassium is separated from chloride of potassium by boiling spirit (as in the first method), and further purified by recrystallisation from water, till it no longer gives a cloud with nitrate of silver.

To obtain the acid from the potassium-salt, the alcoholic solution of this salt is mixed with sulphuric acid; and the liquid filtered from the sulphate of potassium is evaporated as far as possible without decomposition, and, if chloride of potassium be present, till all the hydrochloric acid is driven off. The sulphuric acid is then precipitated from the filtrate by baryta-water, added exactly in the right proportion; the filtrate evaporated as far as possible; and the residue exhausted by boiling ether, which leaves undissolved any salt that may still be present, and on evaporation leaves the acid in the form of a coloured liquid. To decolorise this acid, oxide of lead is dissolved in it, the lead precipitated by sulphuretted hydrogen, and the liquid filtered. The colouring-matter remains with the sulphide of lead, and the filtrate, evaporated *in vacuo*, leaves the crystallised acid.

Dichloromethylsulphurous acid crystallises by evaporation in a vacuum, in small, colourless, deliquescent prisms. Its properties are very much like those of trichloromethylsulphurous acid. It decomposes chlorides, sustains a heat of 140° without alteration, but melts at a higher temperature, with evolution of white vapours and separation of carbon. It is not oxidised by nitric, nitromuriatic, or chromic acid. It dissolves zinc with evolution of hydrogen, forming dichloromethylsulphite, and likewise monochloromethylsulphite of zinc. The quantity of the latter salt is greater as the evolution of hydrogen is kept up for a longer time by continual addition of sulphuric acid; its formation is represented by the equation:

$$2CH^2Cl^2SO^3 \quad + \quad Zn^2 \quad = \quad Zn''Cl^2 \; + \; C^2H^4Cl^2Zn''S^2O^6.$$

The dichloromethylsulphites are soluble in water, some of them also in alcohol. They are distinguished from the chloromethylsulphites by giving off hydrochloric acid by dry distillation, together with sulphurous and carbonic anhydrides; the residue consists of metallic chloride slightly coloured by charcoal:

$$2CHCl^2KSO^3 \quad = \quad 2KCl + C + 2SO^2 + CO^2 + 2HCl.$$

Carbonic oxide is also found among the gaseous products, being probably formed by the action of the free carbon on the carbonic anhydride.

The *ammonium-salt* crystallises by spontaneous evaporation in colourless prisms, permanent in the air, and often an inch long.—The *potassium-salt*, $CHCl^2KSO^3$, forms small pearly scales. It dissolves in water and in boiling alcohol, but not in cold absolute alcohol. It is permanent in the air, neutral to test-papers, and has a slightly saline taste. It bears a heat of 250° without decomposition, but at higher temperatures it is decomposed in the manner above mentioned.—The *silver-salt*, $CHCl^2AgSO^3$, obtained by neutralising the acid with carbonate of silver, is very sensitive to light and heat. When protected therefrom, it may be obtained by evaporation in a vacuum, in small transparent crystals, which may be heated to 150° without decomposing.

TRICHLOROMETHYLSULPHUROUS ACID. $(CCl^3)HSO^3$. *Trichloromethyldithionic* or *Chlorocarbohyposulphuric Acid.* (Kolbe, *loc. cit.*)—Obtained as a potassium—or barium-salt, by gently heating trichloromethylsulphurous chloride, CCl^4SO^2 (p. 559), with potash or baryta; and isolated by decomposing the barium-salt with sulphuric acid, removing the excess of sulphuric acid with carbonate of lead, and the excess of lead by sulphydric acid.

The acid crystallises by evaporation in small colourless prisms, containing $CHCl^3SO^3.H^2O$. The crystals, dried in a vacuum, yield a colourless deliquescent mass, difficult to dry completely. It melts at 130° in its water of crystallisation, and begins to boil at 160°, partly volatilising; while another part is completely resolved into hydrochloric acid, sulphurous oxide, and chloride of carbonyl (phosgene-gas):

$$CHCl^3SO^3 \quad = \quad HCl + SO^2 + COCl^2.$$

It easily dissolves zinc, with evolution of hydrogen, yielding dichloromethylsulphite of zinc. It is not attacked by boiling with fuming nitric, nitromuriatic, or chromic acid. It decomposes all salts of volatile acids, even the chlorides.

The aqueous acid is converted, by a small quantity of potassium-amalgam (1 pt. potassium to 100 pts. mercury), into dichloromethylsulphite of potassium; with a larger quantity of the amalgam, the monochlorinated salt is formed, and with a still larger quantity, the methylsulphite.

The trichloromethylsulphites are soluble in water and in alcohol, and have an astringent metallic taste. When calcined they decompose like the acid, giving off sulphurous oxide and phosgene, and leaving a residue of chloride. The evolution of phosgene distinguishes the trichloromethylsulphites from the monochlorinated and dichlorinated salts.

The *ammonium-salt* forms large regular prisms, permanent in the air, and resolved by heat into sal-ammoniac, sulphurous oxide, and phosgene.—The *potassium-salt*, prepared as above, and purified by recrystallisation, forms thin transparent plates, which have a harsh disagreeable taste, effloresce on exposure to the air, and give off 7·1 per cent (1 at.) water at 100°. It may be heated to 300° without decomposition, but decomposes at a higher temperature in the manner above mentioned. In aqueous solution it is converted by electrolysis, if no free acid is present, into methylsulphite of potassium (p. 555).

The *sodium-salt*, obtained like the potassium-salt, forms thin rhombic tables, which effloresce readily, and are more soluble in water than the potassium-salt.—The *barium-salt*, $C^2Cl^6Ba''S^2O^6.H^2O$, prepared as above, crystallises on cooling from a hot aqueous solution, in small colourless laminæ, but by spontaneous evaporation in tables of larger size. The crystals dried at 100° still retain 3·05 per cent. (1 at.) water, which escapes at 100°.

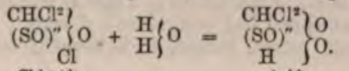
The *lead-salt*, $C^2Cl^6Pb''S^2O^6.2H^2O$, crystallises by spontaneous evaporation of the aqueous solution in broad tables, which redden litmus, and have a sweetish rough taste; they contain 6·1 per cent. (1 at.) of water, which escape at 100°; decomposition begins at 150°. The aqueous solution boiled with oxide of lead, yields an alkaline filtrate, which is precipitated by the carbonic acid of the air, and when evaporated in a vacuum leaves an amorphous basic salt.

The *copper-salt* forms small tables, permanent in the air, and containing 5 at. water, of which only 2 at. go off at 180°—the other three remaining till the salt begins to decompose.

Silver-salt, CCl^3AgSO^3.—The aqueous solution evaporated in a vacuum, and protected from light, yields transparent and colourless prisms, which redden litmus, have a sweetish metallic taste, blacken on exposure to the light, and likewise when their aqueous solution is boiled. But when freed, by heating to 100°, from the 2 at. water of crystallisation which they contain, they remain colourless in sunshine.

Chloromethylsulphurous Chlorides.

Two chlorides are known, derived from di- and tri-chloromethylsulphurous acid, by substitution of Cl for HO. When they are treated with alkalis, the reverse substitution is effected, hydrochloric acid being evolved and the acid produced; *e. g.*:



$$\underset{\text{Chloride.}}{\left.\begin{matrix}CHCl^2\\(SO)''\\Cl\end{matrix}\right\}O} + \left.\begin{matrix}H\\H\end{matrix}\right\}O = \underset{\text{Acid.}}{\left.\begin{matrix}CHCl^2\\(SO)''\\H\end{matrix}\right\}\begin{matrix}O\\O.\end{matrix}}$$

Dichloromethylsulphurous Chloride, $CHCl^2SO^2$. (Kolbe, Ann. Ch. Pharm. liv. 153.—Gerhardt, Compt. chim. 1845, p. 197.)—This compound is formed by the action of reducing agents on trichloromethylsulphurous chloride. When a current of sulphurous oxide gas is passed through an alcoholic solution of the latter body, till the liquid no longer gives a precipitate with water, a solution is formed, containing—besides sulphurous acid—hydrochloric acid, sulphuric acid, and dichloromethylsulphurous chloride:

$$CCl^4SO^2 + SO^2 + 2H^2O = HCl + H^2SO^4 + CHCl^2SO^2.$$

This chloride cannot be completely separated from the bodies with which it is mixed, since it is very easily decomposed by evaporation, yielding phosgene-gas together with sulphuric and sulphurous acids. A small quantity spread out upon a surface soon fills the atmosphere with suffocating vapours of phosgene and sulphurous oxide:

$$CHCl^2SO^2 + O = COCl^2 + SO^2 + HCl.$$

Chlorine passed into the aqueous solution reprecipitates trichloromethylous sulphide.—*Bromine* forms a similar precipitate, containing bromine as well as chlorine.—*Iodine* forms no precipitate. The aqueous solution boiled with *potash* yields chloride and dichloromethylsulphite of potassium.

This compound has not been obtained in the separate state, and therefore its composition has not been determined by analysis. Kolbe assigned to it the formula CCl^2SO^2 (*schwefligsaures Kohlenchlorid*); the more probable view of its composition above given was suggested by Gerhardt. The two formulæ differ only by HCl.

Trichloromethylsulphurous Chloride, CCl^4SO^2. *Sulphite of Perchloride of Carbon. Schwefligsaures Kohlensuperchlorid* (Kolbe). *Chlorunterschwefligsaures Chlorkohlenoxyd* (Berzelius).—This compound, discovered by Berzelius and Marcet (Schw. J. ix. 298), and further examined by Kolbe (Ann. Ch. Pharm. liv. 148), is produced by the action of moist chlorine on carbonic disulphide:

$$CS^2 + 6Cl^2 + 2H^2O = CCl^4SO^2 + SCl^4 + 4HCl.$$

Kolbe prepares it by introducing into a stoppered bottle, having a capacity of about six litres, a quantity of manganic peroxide and hydrochloric acid sufficient to fill about half of it, then adding about 50 grammes of carbonic disulphide, and immediately closing the vessel. The mixture is left for several days in a cool place; then, after frequent agitation, exposed to a temperature of about 30° (most conveniently to the rays of the sun in summer), till the greater part of the carbonic disulphide is transformed. The action is much facilitated by adding from 100 to 200 grms. of commercial nitric acid. All danger of the vessel bursting from internal pressure may be obviated by lifting the stopper from time to time. The mixture is then transferred to a large glass flask, and distilled in an oil-bath into a cooled receiver. Undecomposed carbonic disulphide then passes over first, mixed with a yellowish fetid liquid; and afterwards the trichloromethylsulphurous chloride, which attaches itself in crystals to the sides of the receiver, but is easily detached by slight blows: 50 grms. of carbonic disulphide yield nearly 100 grms. of trichloromethylsulphurous chloride.

This chloride is a white, crystalline, volatile body, insoluble in water and in acids, soluble in alcohol, ether, and carbonic disulphide; its alcoholic solution is precipitated by water. It melts at 135°, and boils without alteration at 170°; distils also with vapour of water. It has an extremely pungent odour, excites tears, and produces a disagreeable roughness in the throat. Its alcoholic solution, when recently prepared, is but slightly clouded by nitrate of silver, precipitation not taking place till the liquid has remained for some time in contact with the air.

The compound sublimes like camphor, in small, colourless, transparent plates, having an adamantine lustre. In the dry state it does not alter the colour of litmus, but reddens it when moist, in consequence of decomposition. The moist crystals are white, opaque, and form vegetations like hoarfrost. It supports a moderately high temperature without decomposition; but when passed through a tube heated to dull redness, it is resolved into chlorine, sulphurous oxide, and perchlorethylene:

$$2CCl^3SO^2 = C^2Cl^4 + 2Cl^2 + 2SO^2.$$

When distilled with a large excess of strong sulphuric acid, it is resolved into sulphurous oxide, hydrochloric acid, and phosgene:

$$CCl^3SO^2 + H^2O = SO^2 + 2HCl + COCl^2.$$

In contact with air and water, it decomposes in a similar manner, yielding hydrochloric acid, sulphurous oxide, sulphuric acid, and carbonic dioxide.

It dissolves in caustic potash, forming trichloromethylsulphite and chloride of potassium.

Naphthylsulphurous Acid, $C^{10}H^8SO^3 = (C^{10}H^7)HSO^3 = \left.\begin{matrix}(SO)''\\ C^{10}H^7.H\end{matrix}\right\}O^2$. *Sulphonaphthalic*, *Hyposulphonaphthalic*, or *Naphthyldithionic Acid.* (Faraday [1827], Ann. Ch. Phys. [2], xxxiv. 164.—Berzelius, *ibid.* lxv. 290.—Wöhler, Ann. Ch. Pharm. xxxvii. 197.—Regnault, Ann. Ch. Phys. [2], lxv. 87.—Laurent, Rev. scient. xiii. 587.—Kimberly, Ann. Ch. Pharm. cxiv. 129.)—This acid is produced, together with naphthylene-sulphurous (disulphonaphthalic) acid, by melting naphthalene with strong sulphuric acid or sulphuric anhydride.—When naphthalene is dissolved to saturation, in strong sulphuric acid heated to 90°, and the solution is exposed to the air, it solidifies completely after some time; and the solidified mass, after being freed from excess of acid by pressure between porous tiles, dissolves completely in water, provided all the naphthalene has been converted into acid products. To separate the two acids, the aqueous solution is neutralised with carbonate of barium, concentrated, and mixed with twice its volume of alcohol, which precipitates naphthylene-sulphite of barium, while the naphthylsulphite remains in solution, and may be crystallised therefrom.—To obtain the free acid, the solution of the barium-salt is precipitated by sulphuric acid; the excess of the latter removed by carbonate of lead; the resulting naphthylsulphite of lead is decomposed by sulphydric acid; and the filtrate is evaporated in a vacuum.

Naphthylsulphurous acid may be obtained, by evaporation of its aqueous or alcoholic solution, as an irregularly crystalline deliquescent mass, containing $C^{10}H^8SO^3.H^2O$. It has a strongly acid, astringent, metallic taste; is extremely soluble in water, oil of turpentine, fixed oils, and alcohol, but very slightly soluble in ether. It melts between 85° and 90°, blackens at about 120°, giving off an odour of naphthalene, and when more strongly heated swells up considerably, leaving a very bulky cinder. The aqueous solution turns brown on boiling.

Naphthylsulphites.—The acid is monobasic. Its salts are soluble in water, for the most part also in alcohol, and have a bitter, almost metallic taste. When heated, they give off a considerable quantity of naphthalene, together with sulphurous oxide, and leave a residue of sulphate and sulphide.—The potassium-salt fused with excess of potassic hydrate is decomposed, with evolution of sulphurous oxide, and formation of a solid body, probably naphthol or naphthylic alcohol. (Wurtz, Compt. rend. lxiv. 750.)

The *ammonium-salt* crystallises in slender needles, permanent in the air. Its solution becomes acid on evaporation. When subjected to dry distillation, it melts, decomposes, and takes fire.—The *potassium-salt*, $2C^{10}H^7KSO^3.H^2O$, crystallises in small, white, very brilliant scales, permanent in the air, and slightly soluble in water.—The *sodium-salt* is similar, and has a strong metallic taste.—The *silver-salt*, $C^{10}H^7AgSO^3$, is moderately soluble, 100 pts. of water at 20° dissolving about 10·3 pts. of it. The solution is not decomposed by boiling.

The *barium-salt*, $C^{20}H^{14}Ba''S^2O^6.2H^2O$, crystallises from a hot saturated solution on cooling, in small tufts or cauliflower-heads; by spontaneous evaporation in irregular scales, grouped like cockscombs. In the dry state it quickly absorbs moisture from the air. It is but sparingly soluble in water, 100 pts. of water dissolving 1·13 pts. of it at 15°, and 4·76 pts. at 100°. It dissolves also in absolute alcohol and in ether. Heated on platinum-foil, it burns with a bright very smoky flame, leaving a blackish residue.—The *strontium-salt* is crystalline.—The *calcium-salt* crystallises with difficulty. When boiled with nitric acid, it yields nitronaphthylsulphite of calcium.—The *magnesium-*, *zinc-*, *nickel-*, *manganous*, and *ferrous* salts are also crystallisable.—The *cupric salt* crystallises in greenish scales containing water, which they partly give off in dry air.—The *neutral lead-salt*, $C^{20}H^{14}Pb''S^2O^6$, crystallises less regularly than the barium-salt. When heated it decomposes, throwing out ramifications in all directions, and increasing considerably in volume. Its solution boiled with oxide of lead yields a basic salt containing $C^{20}H^{14}Pb''S^2O^6.Pb''O$ or $C^{20}H^{14}Pb''S^2O^6.3Pb''O$, according to the quantity of oxide used.—The *mercuric salt*, obtained by dissolving mercuric oxide in naphthylsulphurous acid, is yellow and deliquescent.

Metanaphthylsulphurous Acid.—This name may be applied to an acid, apparently isomeric with naphthylsulphurous acid, which, according to Faraday, is sometimes formed in small quantity in the preparation of the latter, especially when 1 pt. of naphthalene is very strongly heated with 2 pts. of concentrated sulphuric acid, without, however, allowing the mixture to give off sulphurous oxide. On saturating the aqueous solution of the product with carbonate of barium, the barium-salt of this peculiar acid is precipitated, together with sulphate, and may be dissolved out from the latter by boiling water; on evaporating the resulting solution, it is deposited in small hard crystals, slightly soluble in water and in alcohol. This salt contains the same quantity of barium as the ordinary naphthylsulphite, but is distinguished from it by not burning with flame when heated, but merely smouldering (Faraday, Berzelius).—The *potassium-salt* of the same acid crystallises in scales, soluble in water and in alcohol.—The *lead-salt* is very much like the barium-salt. By decomposing it with sulphuretted hydrogen, an acid is obtained, which crystallises in scales, soft to the touch, permanent in the air, but turning brown on exposure to the sun. (Faraday, Berzelius.)

Naphthylsulphurous Chloride, $C^{10}H^7ClSO^2$. (Kimberly, Ann. Ch. Pharm. cxiv. 129.)—Produced by the action of phosphoric pentachloride on naphthylsulphite of sodium dried at 100°. On treating the product with water, and crystallising the undissolved portion from ether free from alcohol, it is obtained pure, in colourless, microscopic, rhombic laminæ. It is inodorous, melts at 65°, and solidifies in globular masses on cooling, but, if kept from agitation and from contact with solid bodies, it remains liquid below 55°. It dissolves very easily in ether, benzol, carbonic disulphide, and phosphoric oxychloride. It is for the most part decomposed by dry distillation, the decomposition beginning at about 120°. It is slowly decomposed by *water*, easily by *potash*, in aqueous and especially in alcoholic solution, yielding alcohol and naphthylsulphurous acid.—*Alcohol* converts it slowly in the cold, quickly when heated, into ethylnaphthylic sulphite:

$$C^{10}H^7ClSO^2 + (C^2H^5)HO = HCl + (C^2H^5)(C^{10}H^7)SO^3.$$

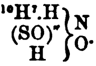
Aqueous *ammonia* converts it into naphthylthionamic acid:

$$C^{10}H^7ClSO^2 + H^3N = HCl + C^{10}H^9NSO^2.$$

Ethylnaphthylic Sulphite, $C^{12}H^{12}SO^3 = \left.\begin{matrix}C^2H^5\\C^{10}H^7\end{matrix}\right\}SO^2$. (Kimberly, *loc. cit.*)—Prepared by heating 1 at. naphthylsulphurous chloride with not more than 2 at. alcohol, in an apparatus so arranged that the vapours may condense and flow back again; then distilling off the excess of alcohol, and washing the residue with water; if the product is coloured, it must be dissolved in ether, and treated with animal charcoal.

Ethylnaphthylic sulphite, when recently prepared, is a viscid liquid at ordinary temperatures, and does not solidify even at −8° to −10°; but after keeping for several days (or, if it has been heated above 50°, after weeks or months), it solidifies in nodules composed of laminar crystals. It is insoluble in water, but mixes in all proportions with alcohol and ether. It is decomposed by distillation, giving off sulphurous oxide, yielding a considerable sublimate of naphthalene, and leaving a small carbonaceous residue.—By aqueous or alcoholic *potash*, it is quickly resolved into alcohol and naphthylsulphite of potassium. In alcoholic solution it is decomposed by water in the same manner as by potash; and when heated with water alone in a sealed tube to about 150°, it is resolved, without blackening or formation of secondary products, into alcohol, naphthalene, and sulphuric acid (probably first into alcohol and naphthylsulphurous acid, which is then further split up into naphthalene and sulphuric acid).—With *pentachloride of phosphorus*, it yields ethylic chloride, naphthylsulphurous chloride, and phosphoric oxychloride:

$$(C^2H^5)(C^{10}H^7)SO^3 + PCl^5 = C^2H^5Cl + C^{10}H^7ClSO^2 + POCl^3.$$

Naphthylthionamic Acid, $C^{10}H^9NSO^2$ = 

$$\left.\begin{array}{c} C^{10}H^7.H \\ (SO)'' \\ H \end{array}\right\} \begin{array}{l} N \\ O. \end{array}$$

Naphthylthionamide.

(Kimberly, *loc. cit.*)—Produced, by triturating naphthylsulphurous chloride with ammonia, as a yellow oil, which solidifies to an amorphous mass. It dissolves easily in ether and in alcohol, and separates from either solution in microscopic crystals, apparently quadratic combinations, P . oP . P∞, with the angle P : P on the lateral edges = 110°. It dissolves also in aqueous ammonia, in strong hydrochloric acid, and in glacial acetic acid, and crystallises from the two latter solutions unaltered. It is inodorous, has a greyish-yellow colour when dry, light-yellow when moistened with aqueous ammonia, gradually turning red on exposure to the air. It melts without decomposition, in boiling water, to a viscid liquid, which solidifies to an amorphous mass; at a higher temperature, it chars and gives off pungent vapours.

It is quickly decomposed by aqueous *potash*, yielding ammonia and naphthylsulphite of potassium. Heated with aqueous *nitrite of potassium*, it gives off nitrogen, and is converted into naphthylsulphite of potassium; part of it is, however, transformed at the same time into a resinous substance, insoluble in water, and detonating slightly when heated.

When the alcoholic solution of the acid, containing a little free ammonia, is mixed with excess of *argentic nitrate*, and the ammonia is allowed to evaporate gradually at ordinary temperatures, argentic naphthylthionamate, $C^{10}H^8AgNSO^2$, is deposited as a white crystalline substance, easily soluble in alcohol, ether, and ammonia, and quickly blackening when exposed to light.

Benzonaphthylthionamic acid, $C^{10}H^8(C^7H^5O)NSO^2$, is produced by fusing naphthylthionamic acid with an equivalent quantity of benzoic chloride, till hydrochloric acid is no longer evolved; and on washing the product with lukewarm water, drying it, and recrystallising from alcohol, it separates in microscopic prismatic crystals, easily soluble in alcohol, ether, aqueous ammonia, and glacial acetic acid. It melts without decomposition at 100°, but decomposes at a higher temperature, and when boiled with aqueous potash, gives off ammonia, and yields benzoate and naphthylsulphite of potassium. When its solution in absolute alcohol is mixed with ammonia and argentic nitrate, and left to evaporate, it deposits argentic benzonaphthylthionamate, $C^{10}H^7Ag(C^7H^5O)NSO^2$, as an amorphous flocculent precipitate, which dissolves somewhat slowly in alcohol, and may be crystallised in microscopic needles by mixing its ammoniacal alcoholic solution with a slight excess of acetic acid, and gently warming the liquid. (Kimberly.)

Bromo-, Chloro-, and Nitro-naphthylsulphurous Acids.

These acids are formed by heating the bromo-, chloro-, and nitro-naphthalenes with fuming sulphuric acid, or (in the case of the monochlorinated compound) with ordinary concentrated sulphuric acid.

Bromonaphthylsulphurous Acid, $C^{10}H^7BrSO^3 = (C^{10}H^6Br)HSO^3$. (Laurent, Compt. chim. 1849, p. 392.)—When the solution obtained by heating bromonaphthalene with fuming sulphuric acid is neutralised with potash, diluted, and boiled, the filtered liquid deposits, on cooling, a crystalline pulp of *potassic bromonaphthylsulphite*, $C^{10}H^6BrKSO^3$, which is colourless, slightly soluble in cold water, moderately soluble in boiling water and alcohol, whence it crystallises in tubercles. Boiling nitric acid converts it into a yellow salt, which takes fire when heated in a close vessel, and probably consists of $C^{10}H^5(NO^2)BrKSO^3$.

A solution of potassic bromonaphthylsulphite poured into a warm moderately concentrated solution of barium-chloride, precipitates the *bromonaphthylsulphite of barium*, $C^{20}H^{12}Br^2Ba''S^2O^6$, as a crystalline salt soluble in cold water. The solution of the potassium-salt forms white precipitates with moderately strong solutions of calcic chloride and plumbic acetate, but does not precipitate the salts of magnesium, manganese, cobalt, nickel, zinc, mercury, and silver.

Dibromonaphthylsulphurous Acid, $C^{10}H^{6}Br^{2}SO^{3} = (C^{10}H^{5}Br^{2})HSO^{3}$. (Laurent, Compt. chim. 1849, p. 392.)—Prepared as above from dibromonaphthalene. —The *potassium-salt*, $C^{10}H^{5}Br^{2}KSO^{3}$, is crystalline, and soluble in boiling alcohol.—The *barium-salt*, $C^{20}H^{10}Br^{4}Ba''S^{2}O^{6}$, is obtained by pouring a solution of the potassium-salt into a boiling and very dilute solution of barium-chloride, and separates, on cooling, as a flocculent precipitate composed of microscopic needles.

Chloronaphthylsulphurous Acid, $(C^{10}H^{6}Cl)HSO^{3}$. (Zinin, J. pr. Chem. xxxiii. 36.)—When a mixture of 2 vols. strong sulphuric acid and 1 vol. chloronaphthalene is heated to 140° for a quarter of an hour, a transparent brownish liquid is obtained, which does not alter on cooling; but is converted, by addition of a few drops of water, into a white, buttery, scarcely crystalline mass, which may be freed from excess of sulphuric acid by spreading it out on a porous tile (Zinin). The same acid appears to be formed, with evolution of hydrochloric acid, on dissolving chloride of naphthalene in fuming sulphuric acid. (Laurent.)

Chloronaphthylsulphurous acid dissolves easily in water and in alcohol; when heated, it melts to a brownish liquid, decomposes, and gives off an odour of naphthalene.

The *ammonium-salt* of this acid is crystalline and very soluble. Its solution forms soluble curdy precipitates with ferrous and argentic salts.—The *potassium-salt* is slightly soluble in water and in alcohol.—The *barium-salt*, $C^{20}H^{12}Cl^{2}Ba''S^{2}O^{6}$, forms microscopic needles of a dull white colour, and very soluble.—The *cupric salt* is bluish and very soluble.—The *ferrous salt* is a white flocculent precipitate.—The *lead-salt* is a white nearly insoluble powder.—The *silver-salt* is a white curdy precipitate, slightly soluble in water, and decomposing at 100°.

Dichloronaphthylsulphurous Acid, $(C^{10}H^{5}Cl^{2})HSO^{3}$. (Zinin, *loc. cit.*)—Prepared like the preceding. It is a white buttery acid, very soluble in water. Its *ammonium-salt* is also very soluble.—The *potassium-salt* and the *barium-salt*, $C^{20}H^{10}Cl^{4}Ba''S^{2}O^{6}$, form small slightly soluble needles.—The *silver-salt*, $C^{10}H^{5}Cl^{2}AgSO^{3}$, crystallises in colourless scales, still less soluble than the potassium-salt.

Trichloronaphthylsulphurous Acid, $(C^{10}H^{4}Cl^{3})HSO^{3}$. (Laurent, Compt. chim. 1849, p. 394.)—Prepared by dissolving trichloronaphthalene in fuming sulphuric acid, neutralising the diluted solution with potash, converting the potassium-salt into a barium-salt, then into a lead-salt, and decomposing the latter with sulphuric acid. The aqueous solution thus obtained solidifies on cooling to a mass of microscopic needles, which may be purified by recrystallisation from boiling alcohol.

The *ammonium-salt* of this acid is easily soluble in water and in aqueous ammonia. Most of the other trichloronaphthylsulphites, even those of potassium and sodium, are but very slightly soluble in cold water; consequently the acid and its ammonium-salt form precipitates even in the cold dilute solutions of the nitrate and sulphite of potassium and sodium, and in those of the chlorides of barium and calcium, and of the sulphates of magnesium, nickel, and copper.

The *potassium-salt* forms opaque microscopic scales, very soluble in boiling water, nearly insoluble in cold water and in boiling alcohol.—The *barium-salt*, $C^{20}H^{8}Cl^{6}Ba''S^{2}O^{6}$, requires from 300 to 400 pts. of boiling water to dissolve it.—An *ammoniacal cupric salt*, $C^{20}H^{8}Cl^{6}CuS^{2}O^{6}.4NH^{3}.4H^{2}O$, is obtained by pouring a solution of the ammonium-salt into cupric acetate, adding ammonia, and heating. The solution, on cooling, solidifies to a filamentous jelly, like the mycodermic substances deposited from tartaric solutions. The washed salt has a lilac colour, changing to blue on drying.

Tetrachloronaphthylsulphurous Acid, $(C^{10}H^{3}Cl^{4})HSO^{3}$. (Laurent, Compt. chim. 1849, p. 397.)—Prepared by heating tetrachloronaphthalene with fuming sulphuric acid.—The *potassium-salt*, $C^{10}H^{3}Cl^{4}KSO^{3}$, is nearly insoluble in cold, slightly soluble in boiling water, very soluble in boiling alcohol, whence it separates in microscopic spherules. Its alcoholic solution does not precipitate acetate of barium, but on addition of water, the liquid coagulates to a gelatinous mass.

Nitronaphthylsulphurous Acid, $C^{10}H^{7}(NO^{2})SO^{3}$. (Laurent, Rév. scient. xiii. 588.)—Nitronaphthalene heated with fuming sulphuric acid, yields a red solution, from which water precipitates more or less unaltered nitronaphthalene. The filtered solution saturated with carbonates yields the nitronaphthylsulphites. The acid is also produced by the action of nitric acid on naphthylsulphurous acid. It crystallises in microscopic rhomboïdal scales. Sulphydrate of ammonium appears to convert it into naphthionic acid (iv. 17).

The nitronaphthylsulphites ignite when heated in close vessels.—The *ammonium-salt* crystallises in needles; the *potassium-salt* by spontaneous evaporation, in irregular crystals.—The *calcium-salt*, $C^{20}H^{12}Ca''(NO^2)^2S^2O^6$, is moderately soluble in water and in alcohol.

Dinitronaphthylsulphurous Acid, $C^{10}H^6(NO^2)^2SO^3$, is formed by the prolonged action of nitric acid on naphthylsulphurous acid.—Its *ammonium-salt*, $C^{10}H^5(NH^4)(NO^2)^2SO^3$, crystallises in yellow needles; it is decomposed by sulphydrate of ammonium, yielding a deposit of sulphur, and a peculiar acid, perhaps nitronaphthionic acid. (Laurent, Compt. rend. xxxi. 537.)

Phenylsulphurous Acid, $C^6H^6SO^3 = (C^6H^5)HSO^3$. *Sulphobenzolic, Sulphobenzenic*, or *Sulphobenzidic Acid*. (Mitscherlich [1834], Pogg. Ann. xxxi. 283, 634.—Stenhouse, Proc. Roy. Soc. xiv. 351.—Wurtz, Compt. rend. lxiv. 749.—Kekulé, *ibid*. p. 752.)—This acid is produced by dissolving benzene in fuming sulphuric acid, diluting with water, filtering to separate any sulphobenzide (p. 486) that may have been formed at the same time, saturating with carbonate of barium, converting the resulting barium-salt into a cupric salt by precipitation with cupric sulphite, purifying the cupric salt by crystallisation, and decomposing it with sulphuretted hydrogen. The acid may also be prepared by gently heating benzene with about an equal volume of ordinary concentrated sulphuric acid; and (according to Stenhouse) this is the best method of obtaining it in large quantities, using 4 vols. sulphuric acid to 5 vols. benzene. Phenylsulphurous acid evaporated to a syrupy consistence, yields a crystalline residue, which decomposes at a higher temperature.

The phenylsulphites or sulphobenzolates, $C^6H^5MSO^3$, are very stable salts, some of them bearing a very high temperature without decomposing. The ammonium-salt, however, decomposes easily at 200°, yielding sulphophenylamide (p. 523), together with sulphurous oxide, ammonia, benzene, and a small quantity of phenylic sulphide; and the sodium- and calcium-salts yield, by dry distillation, phenylic sulphide, $(C^6H^5)^2S$, together with carbonic dioxide and sulphurous oxide. (Stenhouse, iv. 417.)

The phenylsulphites distilled with oxychloride of phosphorus, yield phenylsulphurous or sulphophenylic chloride, $C^6H^5ClSO^2$ (Gerhardt and Chancel). They may be boiled for a long time with excess of aqueous potash without decomposition, but by fusion with potassic hydrate they are resolved into sulphurous acid and phenol (Wurtz, Kekulé):

$$\underset{\text{Potassic phenyl-sulphite.}}{(C^6H^5)KSO^3} + KHO = K^2SO^3 + \underset{\text{Phenol.}}{(C^6H^5)HO.}$$

The *phenylsulphites* of *ammonium*, *potassium*, *sodium*, and *calcium* crystallise easily; the *barium-salt* is obtained only in crystalline crusts; the *zinc-* and *silver-salts* are also crystallisable.—The *cupric salt*, $C^{12}H^{10}Cu''S^2O^6$, forms fine, bulky, hydrated crystals, which give off all their water at 170°. (Mitscherlich.)

Nitrophenylsulphurous acid, $C^6H^5(NO)^2SO^3$, is produced by boiling phenylsulphurous acid with nitric acid.—Its *ammonium-salt*, $C^6H^4(NH^4)(NO^2)SO^3$, is converted by sulphydric acid into phenylsulphamate of ammonium. (Laurent, Compt. rend. xxxi. 538.)

Phenylsulphurous Chloride, $C^6H^5ClSO^2 = \left.\begin{matrix}(SO)''\\ C^6H^5\end{matrix}\right\}\begin{matrix}Cl\\ O\end{matrix}$. *Sulphophenylic* or *Sulphobenzolic Chloride*. (Gerhardt and Chancel, Compt. rend. xxxv. 690.)—Produced by the action of phosphoric oxychloride on a phenylsulphite. To prepare it, benzene is gently heated with an equal volume of strong sulphuric acid, till it is completely dissolved; the liquid, after dilution, is saturated with chalk; the filtered solution of calcic phenylsulphite is exactly decomposed by carbonate of sodium, and the solution of sodic phenylsulphite is filtered and evaporated. This salt having been dried at 150°, is then mixed in a retort by small portions with oxychloride of phosphorus, so as to form a thick pulp. The reaction begins in the cold, and as soon as it ceases, the product is to be distilled as long as any oily matter passes over, and the distillate rectified, collecting apart the latter portions, which distil at 254°. The lower portions contain also a considerable quantity of phenylsulphurous chloride, and may be utilised for the preparation of sulphophenylamide (p. 523).

Phenylsulphurous chloride is a colourless, strongly refracting oil, of specific gravity 1·378 at 23°. It boils at 254°, has a strong odour like that of bitter-almond oil, and fumes slightly in the air. It is scarcely attacked by water, but alkalis instantly convert it into phenylsulphite and chloride of alkali-metal. With aqueous ammonia it yields sal-ammoniac and sulphophenylamide (phenylthionamide).

Phenylsulphurous Hydride, $C^6H^6SO^2$. *Benzylsulphurous Acid*. (Kolbe, Ann. Ch. Pharm. cxix. 153; Jahresb. 1861, p. 627.)—Produced, as a zinc-salt, by the action of zinc-ethyl on phenylsulphurous chloride:

$$2C^6H^5ClSO^2 + Zn''(C^2H^5)^2 = 2C^2H^5Cl + C^{12}H^{10}Zn''S^2O^4.$$

Pure phenylsulphurous chloride is mixed with 3 vols. ether free from water and alcohol, and zinc-ethyl is gradually added to the mixture in a flask filled with dry carbonic dioxide, the liquid becoming hot, and depositing a white powder at each addition. As soon as a portion of the mixture no longer exhibits the smell of the chloride, the pasty mass is to be heated to 100° to expel the ether, and the excess of zinc-ethyl is decomposed by water, which will not dissolve the basic zinc-salt formed in the reaction, even on boiling. On treating it with hydrochloric acid, the whole dissolves, excepting a small quantity of a disagreeably-smelling oil [perhaps $C^6H^4(C^2H^5)SO^2$]; and the decanted liquid, on cooling, deposits phenylsulphurous hydride, in large, mostly stellate prisms, which may be freed from the last traces of the oil by recrystallisation. Its formation from the zinc-salt is represented by the equation:

$$C^{12}H^{10}Zn''S^2O^4 + 2HCl = Zn''Cl^2 + 2C^6H^6SO^2.$$

Phenylsulphurous hydride dissolves slightly in cold, easily in boiling water—freely also in alcohol, and especially in ether. It is inodorous; has a strong acid taste and reaction; cannot be sublimed, melts below 100°, and begins to decompose when heated above 100°. It is oxidised to phenylsulphurous acid, slowly by contact with the air, quickly by nitric acid. By nascent hydrogen (evolved from sulphuric acid by zinc), it is converted into phenylic sulphydrate.

Phenylsulphurous hydride is a monobasic acid, which easily decomposes metallic hydrates and carbonates. According to Kekulé's views of the composition of the aromatic bodies, it may be regarded as benzene-sulphurous acid, $C^6H^5(SO^2H)$, that is as benzene in which 1 at. H is replaced by the sulphurous acid residue, SO^2H; the hydrogen in this residue is still replaceable by metals.

The *ammonium-salt* crystallises in colourless silky laminæ, easily soluble in water, sparingly in alcohol and ether.—The *barium-salt*, $C^{12}H^{10}Ba''S^2O^4$, forms crystalline nodules, easily soluble in water, less soluble in alcohol.—The *cupric salt* separates from a strongly concentrated solution, in yellowish-green laminæ, having a satiny lustre and slightly soluble in alcohol.—The *silver-salt*, $C^6H^5AgSO^2$, separates from a hot aqueous solution on cooling in satiny laminæ, slightly soluble in cold water. The same salt is obtained, as a white curdy precipitate, on mixing the aqueous acid with nitrate of silver.—The *neutral zinc-salt*, $C^{12}H^{10}Zn''S^2O^4$, is obtained by boiling the aqueous acid with zinc-carbonate, or by decomposing the basic salt obtained in the preparation of the acid with carbonic acid, and evaporating the filtrate. It crystallises in oblique rhombic plates with truncated angles, moderately soluble in cold and in hot water.

DIPHENYL-DISULPHUROUS OR DIPHENYL-DISULPHOPHENYLIC ACID, $C^{12}H^{10}S^2O^6$. (Fittig, Ann. Ch. Pharm. cxxxii. 201.)—Formed by dissolving phenyl (iv. 409) in warm concentrated sulphuric acid: the warm much-diluted solution is neutralised with carbonate of potassium; and the sparingly soluble potassium-salt, which separates on cooling, is crystallised several times from water. The acid separated from the lead-salt by sulphuretted hydrogen crystallises by evaporation over oil of vitriol in prismatic deliquescent crystals, which melt at 72·5°, and decompose when heated above 200°. The acid is dibasic.—The *potassium-salt*, $C^{12}H^8K^2S^2O^6$, crystallises in efflorescent prisms or scales, insoluble in alcohol, slightly soluble in cold, more easily in hot water, and decomposing at a red heat.—The *barium-salt*, $C^{12}H^8Ba''S^2O^6$, is a white crystalline precipitate, nearly insoluble in water and in acids.—The *calcium-salt*, $C^{12}H^8Ca''S^2O^6$, is also very difficultly soluble in cold water, and is formed only on heating the solution of the potassium-salt with chloride of calcium.—The *lead-salt* is insoluble in water, but soluble in acids.—The *silver-salt* crystallises in laminæ, more soluble in cold water than the potassium-salt. The salts of other metals do not form precipitates with the solution of the potassium-salt.

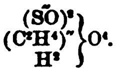
Thymylsulphurous Acid, $C^{10}H^{14}SO^3$. Syn. with CYMYLSULPHUROUS ACID (ii. 298).

Xylylsulphurous Acid, $C^8H^{10}SO^3 = (C^8H^9)HSO^3$. *Sulphoxylenic* or *Sulphoxylolic Acid.* (Cahours, Compt. rend. xxx. 319.—Church, Chem. Soc. Qu. J. xiv. 52.—Völckel, Ann. Ch. Pharm. lxxxvi. 335.—De la Rue and Müller, Chem. Soc. Qu. J. xiv. 54.)—When xylene is left in contact for a week with fuming sulphuric acid, part of it dissolves, and the undissolved portion becomes more or less filled with long, colourless, shining needles of xylylsulphurous acid. They have a strongly acid, afterwards bitter taste; dissolve readily in water and in sulphuric acid; deliquesce quickly on exposure to the air, and may be heated to melting in a vacuum or in vapour of xylene without decomposition; at a higher temperature they become dark-coloured.

Xylylsulphite of barium, $C^{16}H^{18}Ba''S^2O^6$, crystallises in nacreous transparent scales, not altered by boiling with water.

β. Sulphurous Ethers containing Diatomic Alcohol-radicles.

Ethylene-sulphurous Acid, $C^2H^6S^2O^6 = (C^2H^4)H^2(SO^3)^2 =$



$$\left.\begin{matrix}(\overset{''}{SO})^2\\(C^2H^4)''\\H^2\end{matrix}\right\}O^4.$$

Disulphetholic Acid. (Buckton and Hofmann [1856], Chem. Soc. Qu. J. ix. 250; Ann. Ch. Pharm. c. 129.—Husemann, Ann. Ch. Pharm. cxxvi. 269; Jahresb. 1862, p. 428.)—This acid is produced:—1. By heating ethylenic di- or tri-sulphocarbonate (p. 502) with fuming nitric acid:

$$(C^2H^4)COS^2 + 4NO^3H = (C^2H^4)H^2S^2O^6 + 4NO + CO^2 + H^2O.$$
$$(C^2H^4)CS^3 + 6NO^3H = (C^2H^4)H^2S^2O^6 + 6NO + CO^2 + SO^2 + 2H^2O.$$

The liquid is heated as long as nitrous fumes are evolved, then evaporated with repeated addition of water, and neutralised with carbonate of lead; the lead-salt, which crystallises out, is decomposed by sulphuretted hydrogen; and the filtered solution of ethylene-sulphurous acid is evaporated to a syrup. (Husemann.)

2. Together with sulphopropionic acid, by the action of fuming sulphuric acid on propionitrile (cyanide of ethyl) or propionamide:

$$\underset{\text{Propionitrile.}}{C^3H^5N} + 3H^2SO^4 = \underset{\substack{\text{Ethylene-}\\\text{sulphurous}\\\text{acid.}}}{C^2H^6S^2O^6} + \underset{\substack{\text{Acid sulphate}\\\text{of ammonium.}}}{(NH^4)HSO^4} + CO^2.$$

$$\underset{\text{Propionitrile.}}{C^3H^5N} + H^2O + 2H^2SO^4 = \underset{\substack{\text{Sulphopro-}\\\text{pionic acid.}}}{C^3H^6SO^5} + \underset{\substack{\text{Acid sulphate}\\\text{of ammonium.}}}{(NH^4)HSO^4}.$$

Propionamide, (C^3H^7NO), which differs from propionitrile only by H^2O, is acted upon by sulphuric acid in exactly the same manner; and being easier to prepare than propionitrile, is used in preference for the preparation of ethylene-sulphurous acid. For this purpose, a mixture of propionamide with an equal volume of Nordhausen sulphuric acid, is heated as long as carbonic dioxide is evolved and propionic acid distils over. The solid residue is then dissolved in water; the free sulphuric acid is neutralised with finely-pounded marble; the sulphate of ammonium is decomposed by boiling the liquid with carbonate of barium till it no longer gives a permanent precipitate with chloride of barium; and the filtered solution of ethylene-sulphite of ammonium is concentrated to the crystallising-point. To obtain the free acid, this salt is converted into a barium-salt by boiling with baryta-water; the barium-salt is decomposed by sulphuric acid; the acid filtrate is boiled with carbonate of lead; and the resulting lead-salt, after crystallisation, is decomposed by sulphuretted hydrogen. (Buckton and Hofmann.)

The syrupy acid, obtained by carefully evaporating the aqueous solution, solidifies, when left over oil of vitriol, to a radio-crystalline, very deliquescent mass, consisting (according to Husemann) of $C^2H^6S^2O^6.H^2O$. It gives off its 1 at. water at 100°; and the anhydrous acid melts at 94°, and solidifies again at 60° (Husemann); at higher temperatures it chars, and gives off white vapours. (Buckton and Hofmann.)

Ethylene-sulphurous acid is dibasic, forming neutral and acid salts.—The ethylene-sulphites are all soluble and crystallisable.

The *neutral ammonium-salt*, $C^2H^4(NH^4)^2S^2O^6$, crystallises in long monoclinic prisms, often exhibiting the simple combination $\infty P . P\infty$ (Husemann).—The *neutral potassium-salt*, $C^2H^4K^2S^2O^6$, forms thick, four-sided, monoclinic prisms; the *acid potassium-salt*, $2(C^2H^4)HKS^2O^6.3H^2O$, hard, white, crystalline crusts.—The *neutral sodium-salt*, $C^2H^4Na^2S^2O^6$, crystallises in well-defined crystals, belonging to the trimetric system, and exhibiting the combination $\infty P . \breve{P}\infty$.—The *neutral silver-salt*, $C^2H^4Ag^2S^2O^6$, forms thin monoclinic tables; there is also an *acid silver-salt*, $C^2H^5AgS^2O^6.C^2H^4Ag^2S^2O^6$, forming milk-white spherical groups of crystals. (Husemann.)

The *barium-salt*, obtained by boiling the solution of the ammonium-salt with baryta, and precipitating the excess of the latter with carbonic acid, crystallises in stellate groups of six-sided tablets, which contain $C^2H^4Ba''S^2O^6.H^2O$, and become anhydrous at 170° (Buckton and Hofmann).—According to Husemann, a hydrated salt containing $C^2H^4Ba''S^2O^6.2H^2O$, is obtained in small rhombic octahedrons, by saturating the still yellow solution of ethylene-sulphocarbonate in fuming nitric acid with carbonate of barium; whereas the pure acid, saturated in like manner, yields the anhydrous salt, $C^2H^4Ba''S^2O^6$, which is more soluble, and crystallises in slender monoclinic prisms.

The *cupric salt*, $C^2H^4Cu''S^2O^6.4H^2O$, forms light-blue monoclinic prisms, which give off $\frac{5}{8}$ of their water at 100°, and the rest at 170° (Husemann).—The *lead-salt* forms easily soluble crystalline crusts, containing $2C^2H^4Pb''S^2O^6.3H^2O$ (Husemann);

according to **Buckton** and **Hofmann**, it crystallises in thin prisms and four-sided laminæ, and its solution, when quickly evaporated, dries up to a tough gummy mass.—The *magnesium-salt*, $C^2H^4Mg''S^2O^6.6H^2O$, crystallises in colourless, easily soluble, monoclinic prisms and tables, which give off half their water at 100°, and the rest at 180° (**Husemann**).—The *mercuric salt*, $C^2H^4Hg''S^2O^6.6H^2O$, forms long, thin monoclinic prisms; the *mercurous salt*, $C^2H^4Hg^2S^2O^6.H^2O$, forms white crusts, which separate on warming into an acid and a basic salt (**Husemann**).—The *zinc-salt*, $C^2H^4Zn''S^2O^6.6H^2O$, crystallises in nacreous monoclinic tablets, which do not give their last atom of water till heated to 175°. (**Husemann.**)

Appendix to Ethylene-sulphurous Acid: SULPHOPROPIONIC ACID, $C^3H^6SO^5 = C^3H^6O^2.SO^3 = \left.\begin{matrix}(SO)'' \\ (C^3H^4O)'' \\ H^2\end{matrix}\right\}O^3$?—Produced, together with ethylene-sulphurous acid (as above described), by the action of sulphuric acid on propionamide or propionitrile. Its ammonium-salt remains in the mother-liquor of the ethylene-sulphite of ammonium, and may be separated therefrom as a syrupy precipitate by addition of absolute alcohol. On boiling the dilute mother-liquor with carbonate of barium, and concentrating, sulphopropionate of barium, $C^3H^4Ba''S^2O^5$ (at 170°), separates in cubic granules; or if the solution be less concentrated, and left to itself for twenty-four hours, in spherical groups of silky crystals. (**Buckton** and **Hofmann.**)

Methylene-sulphurous Acid, $CH^4S^2O^6 = \left.\begin{matrix}(\overset{\prime\prime}{S}O)^2 \\ (CH^2)'' \\ H^2\end{matrix}\right\}O^4$. *Disulphometholic Acid. Methionic Acid.* (**Liebig**, Ann. Ch. Pharm. xiii. 35.—**Wetherill**, *ibid.* lxvi. 122.—**Strecker**, *ibid.* c. 199.—**Buckton** and **Hofmann**, *ibid.* c. 129; Chem. Soc. Qu. J. ix. 241; Jahresb. 1856, p. 508.)—This acid, discovered by Liebig, is produced: 1. By the action of sulphuric oxide (anhydride) on ethylic ether (**Liebig**, **Wetherill**, **Strecker**).—2. By the action of fuming sulphuric acid on acetamide or acetonitrile (**Buckton** and **Hofmann**). Its mode of formation by this second method is exactly similar to that of ethylene-sulphurous acid from propionamide or propionitrile (p. 566), sulphacetic acid being formed at the same time (p. 475).

To prepare it by the first method (which, however, yields but a small product), sulphuric oxide is passed in the state of vapour, or (preferably) introduced in the solid state, into anhydrous ether contained in a cooled vessel; the resulting solution is shaken up with water; the watery liquid, separated from the ethereal solution of neutral ethylic sulphate, is neutralised with carbonate of barium; the methylene-sulphite of barium thus produced is decomposed by excess of sulphuric acid; the filtered solution is boiled with carbonate of lead; and the resulting lead-salt decomposed by sulphuretted hydrogen. (**Strecker.**)

By evaporating the aqueous solution of methylene-sulphurous acid over the water-bath to a syrup, and leaving it to cool in a vacuum, the acid is obtained as a mass of radiating needles (**Buckton** and **Hofmann**); when left over oil of vitriol, it solidifies in long needle-shaped crystals (**Strecker**). It is very deliquescent, has a very sour taste, and is not decomposed by rather strong heating, by prolonged boiling with nitric acid, or by passing chlorine into its solution.

The **methylene-sulphites**, $(CH^2)M^2S^2O^6$, and $(CH^2)M''S^2O^6$, are easily prepared by digesting the aqueous acid with oxides or carbonates. They are all soluble in water, but insoluble in alcohol.

The *ammonium-salt*, $CH^2(NH^4)^2S^2O^6$, crystallises in needles (**Strecker**); in prisms of 97·45, bevelled at the ends, which bear a heat of 190° without decomposition.—The *potassium-salt* crystallises in shining needles or granules, soluble in 14 pts. of water at 22° (**Buckton** and **Hofmann**).—The *sodium-salt* crystallises in needles (**Strecker**).—The *barium-salt*, $CH^2Ba''S^2O^6.2H^2O$, forms nacreous rectangular plates, which give off their water at 150° (**Buckton** and **Hofmann**); at 140° (**Strecker**).

The *cupric salt*, obtained by precipitating the barium-salt with cupric sulphate, crystallises in blue rhombic prisms, containing $CH^2Cu''S^2O^6.5H^2O$, which effloresce and turn whitish on exposure to the air, and become anhydrous at 100° (**Strecker**). Buckton and Hofmann obtained a cupric salt in green needles.

The *neutral lead-salt*, $CH^2Pb''S^2O^6.2H^2O$, obtained by boiling the acid with carbonate of lead, crystallises in large, transparent, colourless rhombic prisms (in small square laminæ, according to **Buckton** and **Hofmann**), which give off their water at 100°. By boiling this salt with plumbic hydrate, a less soluble *basic salt* is obtained, separating from the cooling solution in colourless crystals, which, after drying over oil of vitriol, appear to consist of $C^2H^2Pb^3S^4O^{12}.H^2O$; they have an alkaline reaction, and absorb carbonic acid from the air. (**Strecker.**)

The *silver-salt*, $CH^2Ag^2S^2O^6$, crystallises in groups of thin needles or broad plates, which may be heated to 150° without decomposition (**Buckton** and **Hofmann**), but blacken slightly when exposed to light (**Strecker**). Its concentrated solution is instantly decomposed by ethylic iodide, yielding argentic iodide, alcohol, and free methylene-sulphurous acid, but no ethereal compound. (**Buckton** and **Hofmann**.)

The *zinc-salt*, which is produced with evolution of hydrogen, by dissolving zinc in the aqueous acid, is difficult to crystallise, and is not precipitated by alcohol. (**Buckton** and **Hofmann**.)

Naphthylene-sulphurous Acid, $C^{10}H^8S^2O^6 = (C^{10}H^6)''H^2S^2O^6$. *Disulphonaphtholic*, *Thionaphthic*, or *Hyposulphonaphtholic Acid*. (**Berzelius**, Ann. Ch. Phys. [2], lxv. 290.—**Laurent**, Compt. chim. 1849, p. 390.—**Dusart**, Compt. rend. lxiv. 859.)—Berzelius obtained this acid in small quantity, together with naphthylsulphurous acid (p. 560), by the action of sulphuric acid on naphthalene; and separated the two by the different solubilities of their barium-salts, the naphthylene-sulphite being the more soluble of the two. On partially saturating the diluted solution with carbonate of barium, the naphthylsulphite separates out first; and on completing the saturation of the remaining liquid, concentrating it over the water-bath, and mixing it with two or three times its volume of alcohol, the naphthalene-sulphite is deposited in granular crystals (**Berzelius**). **Dusart**, by using a larger proportion of sulphuric acid, and applying a stronger heat, has succeeded in converting the whole of the naphthalene into naphthylene-sulphurous acid. For this purpose, 10 pts. of naphthalene are strongly heated with 25 pts. of concentrated sulphuric acid, till a sample of the liquid, saturated with a strong solution of sodic carbonate, remains clear, and no longer deposits a crystalline precipitate of sodic naphthylsulphite. The solution is then diluted with water, and saturated with alkaline carbonate; the greater part of the sulphate removed by crystallisation, and the remainder from the mother-liquor by addition of alcohol. The evaporated solution yields crystals of naphthylene-sulphite, which may be purified by recrystallisation.

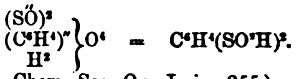
Naphthylene-sulphurous acid, separated from its barium-salt by sulphuric acid, dries up in a vacuum to a brown lamellar mass, having a sour and bitter taste, and soluble in alcohol (Berzelius). The acid is dibasic. The **naphthylene-sulphites**, $C^{10}H^6M^2S^2O^6$ and $C^{10}H^6M''S^2O^6$, resemble the naphthylsulphites; they are very soluble in water, but in general less soluble in alcohol than the naphthylsulphites. They have an acid slightly metallic taste, bear a considerable degree of heat without decomposition, but at very high temperatures give off vapours of naphthalene, with a small quantity of sulphurous oxide (**Berzelius**). They are decomposed by fusion with hydrate of potassium, with formation of metallic sulphite and the potassium-salt of **naphthylenic alcohol**, $C^{10}H^8O^2 = (C^{10}H^6)''H^2O^2$:

$$\underset{\text{Potassic naphthylene-sulphite.}}{C^{10}H^6K^2S^2O^6} + 4KHO = 2K^2SO^3 + 2H^2O + \underset{\text{Potassic naphthylenate.}}{C^{10}H^6K^2O^2}.$$

The naphthylenic alcohol precipitated from its potassium-salt by an acid, and purified from accompanying tarry matter, by solution in water and crystallisation, forms small rhombohedral crystals, soluble in water, and easily soluble in potash. The latter solution instantly burns black in contact with the air, and if afterwards neutralised yields a black precipitate of an acid body, which in strong solutions solidifies to a jelly. (**Dusart**.)

Naphthylene-sulphite of ammonium is obtained, by spontaneous evaporation, as a granular mass; its solution becomes acid when evaporated by heat.—The *potassium-salt* is granular, and slightly soluble in alcohol.—The *barium-salt*, $C^{10}H^6Ba''S^2O^6$, is but slightly soluble in water, even at the boiling heat; very slightly soluble in alcohol; on evaporating the aqueous solution, it remains as an amorphous mass (**Berzelius**).—The *lead-salt*, $C^{10}H^6Pb''S^2O^6.2H^2O$, is very much like the barium-salt, easily soluble in water, but nearly insoluble in alcohol. It retains its 2 at. water at 100°, but gives it up at 220°. (**Laurent**).

Phenylene-sulphurous Acid, $C^6H^6S^2O^6$ =



$$C^6H^6S^2O^6 = \left.\begin{matrix}(S\overset{\prime\prime}{O})^2\\(C^6H^4)''\\H^2\end{matrix}\right\}O^4 = C^6H^4(SO^3H)^2.$$

Disulphobenzolic Acid. (**Buckton** and **Hofmann**, Chem. Soc. Qu. J. ix. 255.)—Produced, together with sulphobenzoic acid (p. 486), by heating benzonitrile (phenylic cyanide) with fuming sulphuric acid. The product, after dilution, is treated with carbonate of barium, as in the preparation of ethylene-sulphurous acid; and the filtered solution of the barium-salts, which is very dark-coloured, is decomposed by sulphuric acid, then boiled with oxide of lead, filtered, and treated with sulphydric acid. The acid liquid is then saturated with carbonate of barium, and the resulting solution treated with alcohol, which throws down first sulphobenzoate, and afterwards phenylene-sulphite of barium.

The acid is, however, more easily obtained by heating phenylsulphurous (sulphobenzolic) acid (p. 563) with fuming sulphuric acid. The product is very dark-coloured, but may be rendered colourless by conversion into a lead-salt, and separation by sulphydric acid. The liquid saturated with carbonate of barium, and evaporated, yields *phenylene-sulphite of barium*, $C^6H^4Ba''S^2O^6$, as an apparently amorphous mass, which, however, appears distinctly crystalline under the microscope. When strongly heated on platinum-foil, it burns, with evolution of sulphurous oxide.

Tritylene-sulphurous or **Propylene-sulphurous Acid,** $C^3H^8S^2O^6 = (C^3H^6)H^2S^2O^6$. *Disulphopropolic Acid.*—Produced, together with sulphobutyric acid, $C^4H^8SO^5$, by heating butyramide with fuming sulphuric acid. The barium-salts of the two acids are both very soluble in water, and very difficult to separate; but on treating the concentrated solution with absolute alcohol, the sulphobutyrate, $C^4H^6Ba''S^2O^5$, separates first; and by continued fractional precipitation with alcohol, a barium-salt is at length obtained, having nearly the composition of the tritylene-sulphite, $C^3H^6Ba''S^2O^6$. By slow evaporation of its aqueous solution, it is obtained in very minute crystals, appearing under the microscope as thin pearly plates. (Buckton and Hofmann, Chem. Soc. Qu. J. ix. 253.)

Sulphuric Compounds.

TRIOXIDE OF SULPHUR. SULPHURIC OXIDE OR ANHYDRIDE, SO^3. *Anhydrous Sulphuric Acid.*—This compound is formed: 1. By the direct oxidation of sulphurous oxide. A perfectly dry mixture of this gas with oxygen, subjected to the action of a rapid stream of electric sparks, slowly diminishes in volume, and deposits sulphuric oxide. The oxidation may also be effected by passing the mixture of the two gases through a red-hot tube containing platinum-black or platinised pumice (Piria, Cimento, ii. 293).—2. By the decomposition of acid sulphates. Acid sulphate of sodium, $NaHSO^4$, heated to dull redness, gives off water, leaving the anhydrosulphate, $Na^2SO^4.SO^3 = 2NaHSO^4 - H^2O$; and this compound, distilled at a higher temperature, gives off white fumes of sulphuric oxide, leaving the neutral sulphate, Na^2SO^4. Ferric, platinic, antimonious, and bismuthic sulphates also give off sulphuric oxide when heated.—3. By the distillation of fuming sulphuric acid. This liquid, prepared at Nordhausen in Saxony, by the dry distillation of dehydrated sulphate of iron, may be regarded as a solution of sulphuric oxide, SO^3, in the strongest sulphuric acid; and when distilled at a gentle heat, gives off the sulphuric oxide in white fumes, while ordinary sulphuric acid, H^2SO^4, remains behind. The sulphuric oxide may be condensed in a dry receiver surrounded by cold water.—4. By distilling strong sulphuric acid with phosphoric oxide (anhydride), sulphuric oxide then passing over, and glacial phosphoric acid remaining behind:

$$H^2SO^4 + P^2O^5 = 2HPO^3 + SO^3.$$

Properties.—Sulphuric oxide crystallises in beautiful white slender needles, arranged in feathery and star-shaped groups, and forming an opaque mass, resembling asbestos. It is tough, and difficult to cut. When recently solidified from the liquid or gaseous state, it melts at about 18°, but quickly passes into another modification, in which it does not melt below 100°, volatilising slowly at the same time, and returning to the first modification (Marignac, Ann. Ch. Pharm. lxxxviii. 228). In the melted state it forms a liquid thinner than oil of vitriol, and probably colourless when pure, but usually exhibiting a brownish colour from the presence of organic matter. It boils at 35°. The specific gravity of the solid oxide is 1·9456 at 13° (Morveau); of the liquid, 1·97 at 20° (Bussy). The density of the vapour is, according to Mitscherlich's observation, 3·01; the calculated density is $\frac{32 + 3 \, . \, 16}{2} \times 0{\cdot}0693 = 2{\cdot}76$.

Reactions.—1. Sulphuric oxide has a most powerful affinity for water, in which it dissolves, forming sulphuric acid. When dropped into water, it hisses like red-hot iron. Wood, paper, and organic bodies in general are quickly carbonised and destroyed by it; when perfectly dry, however, it may be held for a while between the fingers without inconvenience, but it soon absorbs moisture, and then exerts a painful corrosive action.—2. It does not alter the colour of litmus or any other vegetable substance, unless moisture is present.—3. It dissolves without alteration in anhydrous carbonic disulphide, forming a clear solution, which fumes in the air, and solidifies at low temperatures to a deliquescent, interlaced, crystalline mass.

4. Sulphuric oxide is a non-conductor of electricity, and is not decomposed even by the current of a battery of 14 Bunsen's elements. But when dissolved in concentrated sulphuric acid, it is resolved by electrolysis into oxygen at the positive, and sulphur at the negative pole. With certain proportions of the acid and oxide, part of the sulphur, instead of being separated in the free state, reduces the sulphuric acid to sulphurous

acid, and sulphurous oxide is evolved at the negative pole. (Geuther, Ann. Ch. Pharm. cix. 130.)

5. The vapour of sulphuric oxide is resolved, at a strong red heat, into sulphurous oxide and oxygen, 2 vols. SO^3 yielding 2 vols. SO^2 and 1 vol. oxygen.—6. *Phosphorus* takes fire in the vapour at ordinary temperatures, and precipitates the sulphur in the form of a thick crust (Vogel).—7. When *phosphoretted hydrogen-gas* is passed over sulphuric oxide at ordinary temperatures, sulphurous oxide is abundantly evolved, and the sides of the vessel become coated with red oxide of phosphorus [? amorphous phosphorus] (H. Rose).—8. Dry *sulphydric acid* decomposes sulphuric oxide, with formation of sulphuric acid, and separation of sulphur, which partly dissolves, with blue colour, in the sulphuric acid (Geuther):

$$4SO^3 + 3H^2S = 3H^2SO^4 + S^4.$$

9. Metallic *mercury*, heated with sulphuric oxide, abstracts part of the oxygen, forming sulphurous oxide and mercuric oxide, which unites with undecomposed sulphuric oxide, forming mercuric sulphate.—Red-hot *iron* decomposes the vapour, forming sulphide of iron and ferroso-ferric oxide; *zinc*, under similar circumstances, forms sulphide and oxide of zinc. (Albert d'Heureuse, Ann. Ch. Pharm. lxviii. 242.)

10. When sulphuric oxide vapour is passed over anhydrous *baryta* or *lime* heated to low redness, combination takes place, attended with vivid incandescence, and the base is converted into sulphate.

11. When dry *monosulphide of potassium* is brought in contact with an excess of fused sulphuric oxide, an energetic action takes place, resulting in the formation of anhydrosulphate of potassium and sulphuric oxide:

$$5SO^3 + K^2S = K^2SO^4.SO^3 + 4SO^2.$$

Galena is slowly converted by the liquid oxide into sulphate of lead, while sulphurous oxide and sulphur are set free, the latter dissolving in the excess of sulphuric oxide and forming a blue liquid:

$$2SO^3 + Pb''S = Pb''SO^4 + SO^2 + S.$$

Native *sulphide of antimony* dissolves more quickly, with blue coloration and formation of sulphurous oxide and antimonious sulphate, which separates as a basic salt on dilution.—Ferrous sulphide, iron pyrites, and copper pyrites do not act on fused sulphuric oxide. (Geuther, Ann. Ch. Pharm. cxi. 177.)

12. With *pentachloride of phosphorus*, sulphuric oxide yields oxychloride of phosphorus and sulphuric chloride (Schiff, Ann. Ch. Pharm. cii. 111):

$$SO^3 + PCl^5 = POCl^3 + SO^2Cl^2.$$

13. Sulphuric oxide dissolves *sulphur* in various proportions, forming a brown, a green, and a blue liquid, the first of which contains the largest and the last the smallest quantity of sulphur. These solutions are formed by placing flowers of sulphur and sulphuric oxide in alternate layers in a glass tube, sealing it, and heating it to 16°—19°. They are decomposed by water, yielding sulphuric and sulphurous acids and free sulphur. (Wach, Schw. J. l. 1.)

14. Sulphuric oxide unites with a tenth of its weight of *iodine*, forming a compound of a fine green colour, which may be crystallised.

15. Vapour of *nitric peroxide* is rapidly absorbed by sulphuric oxide; and if the action be moderated at first, by passing the vapour slowly and cooling the vessel, and finally assisted by gentle heating till the sulphuric oxide becomes saturated, a white crystalline mass is formed, fusible without decomposition at a gentle heat, and agreeing nearly in composition with the formula $NO^2.SO^3$. When strongly heated, it decomposes, with evolution of oxygen, and a small quantity of nitric peroxide; and if the heating be discontinued as soon as the evolution of oxygen ceases, there remains a hard crystalline compound, similar in appearance to the former, but consisting of $N^2O^3.2SO^3 = 2(NO^2.SO^3) - O$ (Weber, Pogg. Ann. cxxiii. 337; Jahresb. 1864, p. 155).—This latter compound, which may be regarded as anhydrosulphate of nitrosyl or azotyl, $(NO)^2SO^4.SO^3$, is likewise obtained, according to De la Provostaye (Ann. Ch. Phys. [2], lxxiii. 362), by passing the vapour of nitric peroxide into liquid sulphurous oxide:

$$2SO^2 + 4NO^2 = (NO)^2S^2O^7 + N^2O^3;$$

and, according to Brüning (Ann. Ch. Pharm. xcviii. 377), by the action of nitric oxide on sulphuric oxide:

$$3SO^3 + 2NO = (NO)^2S^2O^7 + SO^2.$$

16. A compound of sulphuric oxide with *nitrous chloride*, $NOCl.SO^3$, is obtained by passing the vapours evolved from nitromuriatic acid, and dried by chloride of calcium, over sulphuric oxide till it is saturated. This compound is white and

lamino-crystalline, like stearic acid. When gently heated, it melts without coloration, but at a higher temperature, turns yellow and decomposes. With water it yields sulphuric acid, hydrochloric acid, and the decomposition-products of nitrous acid. In strong sulphuric acid it dissolves, with evolution of hydrochloric acid; and on heating the solution, a liquid distils over, consisting essentially of sulphuric chlorhydrate, SO^3HCl. (Weber, Pogg. Ann. cxxiii. 233.)

17. Dry *ammonia-gas* is absorbed by sulphuric oxide, forming sulphamate of ammonium, $N^2H^6SO^3$ (p. 476).

Sulphato-iodic Oxide or *Anhydride*, $I^2O^5.SO^3$.—This compound is formed by the prolonged action of dry sulphurous oxide on pulverised iodic oxide (I^2O^5) at 100°. A small quantity of iodine is at first liberated, and the iodic oxide is then converted into a light-yellow granulo-crystalline mass, which is quickly decomposed by water, with separation of iodine. By absolute alcohol it is quickly resolved into sulphuric and iodic oxides. With alcoholic potash it forms iodate and sulphate of potassium. Strong sulphuric acid does not act upon it at ordinary temperatures; hydrochloric acid dissolves it, with evolution of chlorine, and formation of chloride of iodine. (Kämmerer, J. pr. Chem. lxxxii. 72; Jahresb. 1861, p. 134.)

Sulphato-acetic Oxide or *Anhydride*.—Vapour of sulphuric oxide is absorbed by cooled acetic oxide, forming a yellow gummy mass, which dissolves in water; the solution, when neutralised with baryta-water and filtered, yields crystals of baric sulphacetate. (Schützenberger, Compt. rend. liii. 538; Jahresb. 1861, p. 439.)

Sulphuric oxide unites with *acetic acid*, *benzoic acid*, and many other organic acids, forming sulphacetic acid, $C^2H^4O^2.SO^3$, sulphobenzoic acid, $C^7H^6O^2.SO^3$, &c.; and with many *hydrocarbons*, forming sulphoacids, which may be regarded as sulphurous ethers (p. 550): *e.g.*, with benzol, C^6H^6, it forms sulphobenzolic or phenylsulphurous acid, $C^6H^6SO^3 = (SO)''.C^6H^5O.HO$, &c.

Chlorosulphuric Oxide or *Anhydride*, $S^2O^5Cl^2$.—This compound, first obtained by H. Rose, by the action of sulphuric oxide on disulphide of chlorine (p. 535), is also produced, according to Rosenstiehl (Compt. rend. liii. 658), by heating sulphuric oxide with dry pulverised chloride of sodium, distilling, and rectifying, to remove the last traces of sulphuric oxide. It is a colourless oil, of specific gravity 1·762 (Rosenstiehl); 1·818 at 16° (Rose); boiling at 145° (Rose), between 145° and 150° (Rosenstiehl). It is violently decomposed by water, and quickly chars organic bodies. With manganates it evolves chlorine; with alkaline chromates it forms chromic oxychloride, CrO^2Cl^2:

$$\underset{\substack{\text{Potassic}\\\text{chromate.}}}{K^2CrO^4} + \underset{\substack{\text{Chlorosul-}\\\text{phuric oxide.}}}{S^2O^5Cl^2} = \underset{\substack{\text{Potassic}\\\text{anhydro-}\\\text{sulphate.}}}{K^2S^2O^7} + \underset{\substack{\text{Chromic}\\\text{oxychloride.}}}{CrO^2Cl^2}.$$

With dry acetate of sodium, it forms chloride of acetyl. (Rosenstiehl.)

SULPHURIC ACID, $H^2SO^4 = H^2O.SO^3 = \left.\begin{matrix}(SO^2)''\\H^2\end{matrix}\right\}O^2 = (SO^2)''.HO.HO$.—This highly important acid is produced, as already observed, by the hydration of the anhydride; by the decomposition of sulphuric chloride; by the oxidation of sulphur, sulphydric acid, and sulphurous acid; and by the decomposition of the polythionic acids (p. 540).

Preparation.—By *the oxidation of Sulphurous Acid*.—Sulphuric acid is produced by passing moist sulphurous oxide and air through tubes containing spongy platinum heated to low-redness. Sulphurous acid is also slowly converted into sulphuric acid by mere exposure to air, and immediately by treatment with powerful oxidising agents. The enormous quantities of sulphuric acid manufactured in this country (more than 100,000 tons annually), are made by burning sulphur or roasting pyrites, and oxidising the resultant sulphurous vapour by means of moist air and certain oxides of nitrogen. For this purpose, the sulphurous acid vapour is mixed with vapour of nitric acid evolved by decomposing a nitrate with sulphuric acid. This acid immediately converts a portion of the sulphurous acid into sulphuric acid, and is itself reduced to nitric oxide, NO; and this gas coming in contact with air, is converted into nitric peroxide, NO^2, which reacts with another portion of sulphurous oxide and with water, in such a manner as to form sulphuric acid and nitric oxide:

$$NO^2 + SO^2 + H^2O = H^2SO^4 + NO.$$

The nitric oxide thus liberated again absorbs oxygen to form nitric peroxide, which again oxidises the moist sulphurous vapours into sulphuric acid, with liberation of nitric oxide, and so on continuously. Theoretically, therefore, a small quantity of nitric oxide should suffice to produce an indefinitely large amount of sulphuric acid. Sometimes, when there is but a small quantity of water present, the sulphurous oxide and nitric peroxide react in the manner already mentioned (p. 570), producing anhydrosulphate of nitrosyl, $(NO)^2S^2O^7$, which, together with certain other sulphates of nitrosyl, formed from it by the action of water and of the sulphuric acid already produced, is deposited as a white crystalline mass on the sides of the vessel or chamber in which the reaction takes place. The formation of these crystalline compounds is not, however, a necessary stage in the process, and in fact, when steam is largely introduced into the chamber (as in the present mode of making the acid), it does not take place at all.

The exact changes which nitric oxide, sulphurous oxide, oxygen, and water undergo, in presence of one another, have been minutely studied by several chemists, particularly by Provostaye and Desains, but without any very definite results. The description above given must indeed be considered rather as a general than a strictly accurate account of the reaction. (See *Gmelin's Handbook*, ii. 445—451; also Weber, Jahresb. 1863, p. 738; 1865, p. 93; Bull. Soc. Chim. 1867, i. 151.)

In the manufacture of sulphuric acid on the large scale, sulphur is burnt slowly on an iron plate forming the floor of a sort of furnace, the amount of air admitted being regulated by means of a smaller iron plate forming the door of the furnace, so that the sulphur when once ignited may go on burning and producing sulphurous oxide with tolerable uniformity. Upon the iron plate on which the sulphur is burnt is also placed an iron pot containing a mixture of nitrate of sodium and sulphuric acid, which continues to generate nitric acid for some time. The sulphurous oxide and nitric acid vapour, from one or several furnaces, are conveyed by means of flues into a large leaden chamber having a capacity of from 50,000 to 100,000 cubic feet or more. Within this chamber, into which steam is admitted continuously by several jets, the reaction chiefly occurs. The nitric acid is soon reduced to nitric oxide, after which the succession of changes already pointed out takes place; and dilute sulphuric acid collects on the floor of the chamber, whence it is drawn off into leaden evaporating pans. The vapours escaping from the large chamber are usually passed into one or two smaller subsidiary chambers also supplied with steam. In these a further condensation occurs, and a still weaker acid is produced, which is run back into the large chamber to become more concentrated. In some manufactories, the vapours from the subsidiary chambers are then passed through coke-scrubbers—that is, through columns packed with coke, over which water is constantly pouring; and here a further condensation occurs, and a very dilute acid is produced, which is pumped up into the subsidiary leaden chambers. In a few factories, Gay-Lussac's scrubber is used instead of the water-scrubber. The coke in this case is kept moistened with concentrated sulphuric acid, which completely absorbs the nitric oxide gas. The acid is then pumped into a second similar scrubber, in which it is robbed of its nitric oxide by means of the sulphurous oxide proceeding from the burning sulphur. In a theoretically perfect operation, there should be no final escape into the atmosphere of any other gas than the nitrogen of the air admitted into the furnace, and thence into the chamber; but in practice a small quantity of sulphurous or nitrous gas, or both, escapes condensation, although the amount of sulphuric acid finally produced usually approximates very closely to the theoretical quantity.

The acid withdrawn from the leaden chambers has generally a specific gravity of about 1·55. By evaporation in a series of shallow leaden pans, its specific gravity is raised to above 1·7. This acid is usually dark-coloured, from the presence of organic matter, and is technically known by the name of "brown acid." The further concentration has to be effected in retorts of glass or platinum. With glass retorts the operation is intermittent. A number of large glass retorts are heated on a sand-bath until the requisite concentration is attained. Throughout the process, a diluted sulphuric acid, containing sulphurous acid from the reaction of the organic matter and sulphuric acid, distils over. This is returned to the leaden chamber, and the concentrated colourless acid is siphoned off from the retorts into carboys. With a platinum retort the process it continuous. Brown acid is constantly admitted at the top, concentrated acid withdrawn from the bottom, and diluted sulphuric acid, with sulphurous acid, distilled off into receivers, whence it is pumped back into the chambers. In commerce, the concentrated colourless acid, having a specific gravity reaching to 1·842, or approximating very closely thereto, is alone known by the name of "oil of vitriol."

The process above described is substantially the same as that introduced by Dr. Roebuck about the year 1720. It is known as the English mode of manufacture, and the product is called "English oil of vitriol." This oil of vitriol always contains lead, and not unfrequently other impurities, chiefly arsenic and nitrous or nitric acid. By diluting it with water, the lead is thrown down as a white precipitate, which becomes black by the action of sulphuretted hydrogen. The arsenic may be recognised by Reinsch's or Marsh's tests, or by neutralising the diluted acid with carbonate of potassium, filtering from the resulting sulphate of potassium, and treating the acidulated filtrate with sulphuretted hydrogen, when a yellow precipitate will be produced. The nitrous or nitric acid can be detected by pouring in a dilute solution of sulphate of iron, so as to float on the top of the acid. Where the two liquids meet, a brownish-purple ring of discoloration will be produced. The addition of sulphide of barium to arsenical sulphuric acid produces a precipitate of mixed sulphide of arsenic and sulphate of barium, which may be separated by subsidence and decantation. The acid may be purified from arsenic by heating it nearly to the boiling-point, and passing a current of hydrochloric acid gas through it; whereby the arsenic is carried over as volatile chloride of arsenic, while the nitric and nitrous acids are expelled almost completely.[*] The nitrous or nitric acid may also be entirely decomposed into water and nitrogen-gas, by heating the acid with a little sulphate of ammonia; and, lastly, by distilling the sulphuric acid after the separation of the arsenic and nitrous acid, it may be obtained quite pure. The distillation must be effected in large retorts, heated, not at the bottom, but somewhat at the sides, to avoid the violent percussive ebullition which results from directly heating the deposit of sulphate of lead which gradually forms at the bottom of the retort. The vapour of oil of vitriol has a very small latent heat, and, under any circumstances, the ebullition of the acid is somewhat percussive. The presence of platinum-clippings in the retort prevents this action to a considerable extent.

According to **Nicklès** (Compt. rend. xlv. 250; Jahresb. 1857, p. 119), commercial oil of vitriol often contains hydrofluoric acid, but may be freed therefrom by diluting it with twice its bulk of water, and gently heating it for about fifteen hours—the hydrofluoric acid then volatilising.

For further details respecting the manufacture, purification, and concentration of sulphuric acid, see Richardson and Watts's *Chemical Technology*, vol. i. pt. i. pp. 51–117, and pt. v. pp. 198–222.

Properties and Reactions.—Pure oil of vitriol, or normal sulphuric acid, H^2SO^4, is a heavy, oily, colourless, inodorous liquid, having a specific gravity of 1·842. It boils at 327°, and freezes at $-35°$. It is very hygrometric, and, when exposed to moist air, will even double its weight in the course of a few days. Hence it is in constant requisition as a desiccating agent. It abstracts water from many organic substances, and thereby gives origin to new compounds. Thus alcohol, acetone, formic acid, glycerin, &c., when dehydrated by sulphuric acid, produce olefiant gas, mesitylene, carbonic oxide, and acrolein respectively. In many cases, the organic substances acted upon by sulphuric acid are completely broken up or destroyed; as is especially the case with woody fibre, sugar, and bodies of allied composition, which, by the loss of water, become thoroughly charred or carbonised. This charring effect of strong sulphuric acid is highly characteristic. The diluted acid slowly destroys organic fibres, without charring them. But tissues, moistened with dilute sulphuric acid and then heated, become charred from the concentration of the acid which gradually takes place. The admixture of the strong acid with water is attended by a great development of heat. On mixing 4 parts by weight of oil of vitriol with 1 part of water, the temperature rises from 0° to 100°. The cooled mixture of water and acid occupies a volume considerably less than that of the two separate liquids.

Sulphuric acid is reduced to sulphydric acid by passing its vapour, with excess of *hydrogen*, through a tube heated to redness.—*Phosphorus* takes fire in sulphuric acid vapour, and liberates sulphur. At increased temperatures, not only *zinc*, *iron*, *copper*, *mercury*, *silver*, and most of the metals save gold and platinum, but also *charcoal* and *sulphur*, exert a reducing action upon strong sulphuric acid, and evolve sulphurous acid. All the metals of the zincic and ferric families, with the exception of copper, readily displace hydrogen from the diluted acid to form their respective sulphates of metal. At ordinary or somewhat increased temperatures, sulphuric acid decomposes the salts of nearly all other acids, with production of the corresponding sulphates, and liberation of the respective acids. By its action on certain highly-oxidised metallic compounds, such as the peroxides of lead and manganese, and the manganic, chromic, and ferric acids, or their salts, it produces sulphates of the respective metals, with evolution of oxygen-gas. Sulphuric acid, like the anhydride, absorbs nitric oxide gas, forming a crystalline sulphate of nitrosyl (p. 577), which dissolves unchanged in an excess of acid. The vapour of sulphuric acid is decomposed, at a red heat, into water, sulphurous oxide, and oxygen.

Sulphuric acid reacts with a large number of hydrogenised bodies, alkaline, neutral and acid, to form new compounds by the elimination of water. The typical reactions are the following:

$$(1.)\quad H^2SO^4 + 2A - 2H^2O = X.$$

In accordance with this reaction, the neutral sulphates of ethyl and phenyl, also sulphobenzide and sulphonaphthalene, are formed by the action of sulphuric acid upon alcohol, phenol, benzene, and naphthalene, respectively. All these products are neutral in their properties.

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[*] On the preparation of sulphuric acid free from arsenic, for medico-legal purposes, see **Bloxam** (Chem. Soc. Qu. J. xv. 52); also **Buignet** and **Bussy** (J. Pharm. [3] xliv. 177; xlvi. 252; Jahresb. 1863, p. 151; 1864, p. 144).

$$(2.)\quad H^2SO^4 + A - H^2O = Y.$$

In accordance with this reaction, sulphanilic acid, ethylsulphuric acid, phenylsulphuric acid, phenylsulphurous acid, and naphthylsulphurous acid are formed by the action of sulphuric acid upon aniline, alcohol, phenol, benzene, and naphthalene, respectively. All these products have the properties of monobasic acids. Sulphuric acid also reacts, in accordance with the above equation, upon benzoic and other monobasic acids; but then the products of its action (sulphobenzoic acid, for instance) have the properties of dibasic acids. The rule which applies to all such reactions as those now under consideration, is that the basicity of the product equals the sum of the basicities of the reagents, minus as many units of basicity as there are atoms of water eliminated (see ACIDS, i. 49).

$$(3.)\quad 2H^2SO^4 + A - 2H^2O = Z.$$

In accordance with this reaction, methylene-sulphurous, ethylene-sulphurous, naphthylene-sulphurous, and phenylene-sulphurous acids (p. 551), also disulphanilic acid (p. 479), have been obtained. Agreeably to the above rule, all these products have the properties of dibasic acids. In the actual reactions, Nordhausen acid, or even sulphuric anhydride, is frequently employed.

Hydrates of Sulphuric Acid.—There are two, if not more, well-defined hydrates of sulphuric acid—namely, the monohydrate, $H^2SO^4.H^2O$, and the dihydrate, $H^2SO^4.2H^2O$. The first compound has a specific gravity of 1·78, and solidifies at 8° or 9°, forming a mass of colourless six-sided prisms, whence it is called glacial sulphuric acid. It boils at 205°—210°, giving off a weak acid vapour. It may be obtained by evaporating any dilute sulphuric acid at a temperature of 205°, until it ceases to lose water. The second hydrate results from the mixture of 1 at. oil of vitriol with 2 at. water. This proportion corresponds with the maximum condensation (nearly 8 per cent.) which results from the union of the acid and water. Its specific gravity is 1·62. It boils at 193°, giving off nothing but water until the temperature rises to 205°. It may be obtained by evaporating any more dilute acid at 100°, until it ceases to lose water. Both these hydrates dissolve snow with production of intense cold.

Fuming Sulphuric Acid.—This is a mixture or compound of sulphuric acid and sulphuric anhydride, obtained by the decomposition by heat of certain sulphates. The anhydrosulphates of the alkali-metals, $M^2SO^4.SO^3$, and the sulphates of the triatomic metals—iron (ferricum), bismuth, antimony, &c.—when subjected to dry distillation, give off sulphuric oxide or anhydride (p. 569), and if moisture is present, part of this compound is converted into sulphuric acid. At Nordhausen, in Saxony, an impure ferric sulphate, obtained by exposing ferrous sulphate (green vitriol) to a moderate heat in contact with the air, is distilled in earthern retorts arranged in a reverberatory furnace; and the distillate, consisting chiefly of sulphuric anhydride, is received in a small quantity of water or, more frequently, in ordinary oil of vitriol. The product thus obtained is a heavy brown oily liquid, known as Nordhausen, or Saxon, or fuming oil of vitriol. It has a specific gravity of 1·9, a composition corresponding nearly with the formula $H^2S^2O^7$, or $H^2SO^4.SO^3$, and is probably a definite compound analogous to the metallic anhydrosulphates above mentioned. It solidifies at 0°, forming colourless transparent crystals. When gently heated, it breaks up into sulphuric oxide, SO^3, which distils over, and sulphuric acid, H^2SO^4, which remains.

According to R. Müller (Ann. Ch. Pharm. cxxii. 1; Jahresb. 1862, p. 93), a crystalline compound of this acid with nitric peroxide, containing $H^2S^2O^7.N^2O^4$, is produced by the action of nitric peroxide in excess on ordinary concentrated sulphuric acid: $2H^2SO^4 + 2NO^2 = H^2S^2O^7.N^2O^4 + H^2O$. It dissolves in concentrated more readily than in dilute sulphuric acid, and separates unaltered on diluting the former solution with water.

Uses of Sulphuric Acid.—Sulphuric acid is the starting-point of nearly all important chemical manufactures. It is largely used in the preparation of nitric acid from the nitrates of potassium and sodium, of hydrochloric acid and chlorine from chloride of sodium, and consequently in the preparation of various bleaching compounds. Superphosphate of lime and artificial manures generally, of which many thousand tons are annually consumed in this country, are made by the action of sulphuric acid on bones, coprolites, &c. But the greatest consumption of this acid is in the manufacture of sulphates, especially of sulphate of sodium from the chloride, which is the first step in the manufacture of commercial soda or carbonate of sodium. It is also largely used for dissolving silver-alloy. The fuming acid is used chiefly for dissolving indigo, the solution constituting the important dyestuff called Saxony-blue (iii. 258). (Odling's *Manual of Chemistry.*)

Otto's Table of the Strength of Sulphuric Acid of different Densities at the Temperature of 15° C.

Per cent. of H^2SO^4.	Specific Gravity.	Per cent. of SO^3.	Per cent. of H^2SO^4.	Specific Gravity.	Per cent. of SO^3
100	1·8426	81·63	50	1·398	40·81
99	1·8420	80·81	49	1·3866	40·00
98	1·8406	80·00	48	1·3790	39·18
97	1·8400	79·18	47	1·3700	38·36
96	1·8384	78·36	46	1·3610	37·55
95	1·8376	77·55	45	1·3510	36·73
94	1·8356	76·73	44	1·3420	35·82
93	1·8340	75·91	43	1·3330	35·10
92	1·8310	75·10	42	1·3240	34·28
91	1·8270	74·28	41	1·3150	33·47
90	1·8220	73·47	40	1·3060	32·65
89	1·1860	72·65	39	1·2976	31·83
88	1·8090	71·83	38	1·2890	31·02
87	1·8020	71·02	37	1·2810	30·20
86	1·7940	70·10	36	1·2720	29·38
85	1·7860	69·38	35	1·2640	28·57
84	1·7770	68·57	34	1·2560	27·75
83	1·7670	67.75	33	1·2476	26·94
82	1·7560	66·94	32	1·2390	26·12
81	1·7450	66·12	31	1·231	25·30
80	1·7340	65·30	30	1·223	24·49
79	1·7220	64·48	29	1·215	23·67
78	1·7100	63·67	28	1·2066	22·85
77	1·6980	62·85	27	1·1980	22·03
76	1·6860	62·04	26	1·1900	21·22
75	1·6750	61·22	25	1·1820	20·40
74	1·6630	60·40	24	1·1740	19·58
73	1·6510	59·59	23	1·1670	18·77
72	1·6390	58·77	22	1·1590	17·95
71	1·6370	57·95	21	1·1516	17·14
70	1·6150	57·14	20	1·1440	16·32
69	1·6040	56·32	19	1·1360	15·51
68	1·5920	55·59	18	1·1290	14·69
67	1·5800	54·69	17	1·1210	13·87
66	1·5780	53·87	16	1·1136	13·06
65	1·5570	53·05	15	1·1060	12·24
64	1·5450	52 24	14	1·0980	11.42
63	1·5340	51·42	13	1·0910	10·61
62	1·5230	50·61	12	1·0830	9·79
61	1·5120	49·79	11	1·0756	8·98
60	1·501	48·98	10	1·0680	8·16
59	1·490	48·16	9	1·0610	7·34
58	1·480	47·34	8	1·0536	6·53
57	1·469	46·53	7	1·0464	5·71
56	1·4586	45·71	6	1·0390	4·89
55	1·448	44·89	5	1·0320	4·08
54	1 438	44·07	4	1·0256	3·260
53	1·428	43·26	3	1·0190	2·445
52	1·418	42·45	2	1·0130	1·630
51	1·408	41·63	1	1·0064	0·816

For other tables of the strength of sulphuric acid, see Richardson and Watts's *Chemical Technology,* vol. i. pt. v. pp. 815–820.

Derivatives of Sulphuric Acid.

Sulphuric Bromide, SO^2Br^2. *Bromide of Sulphuryl. Bromosulphuric Acid.* —Prepared like the corresponding chlorine-compound. It is a white crystalline body, which volatilises at ordinary temperatures, and when heated in a sealed tube with excess of silver-sulphate, yields silver-bromide and sulphuric oxide, $SO^2Br^2 + Ag^2SO^4 = 2AgBr + SO^3$. (Odling and Abel, Chem. Soc. Qu. J. vii. 2.)

Sulphuric Chlorhydrate, $HClSO^3 = (SO^2)''\left\{\begin{matrix}Cl\\HO\end{matrix}\right.$. *Chlorhydrosulphurous Acid.* (A. W. Williamson, Proc. Roy. Soc. vii. 11.)—This compound, derived from sulphuric acid, $(SO^2)''.HO.HO$, by the substitution of 1 at. Cl for 1 at. HO, is the first product of the action of phosphoric pentachloride upon strong sulphuric acid:

$$(HO)^2SO^2 + PCl^5 = Cl(HO)SO^2 + HCl + POCl^3.$$

It is also produced by the action of water on sulphuric chloride:

$$Cl^2SO^2 + H^2O = Cl(HO)SO^3 + HCl;$$

by the direct combination of hydrochloric acid gas and sulphuric oxide; and by the action of platinum-black on an imperfectly dried mixture of chlorine and sulphurous oxide. It appears also to be identical with the compound which H. Rose obtained by distilling disulphide of chlorine with fuming sulphuric acid (p. 535).

Sulphuric chlorhydrate is a colourless liquid, which boils at 145°, and is at the same time partially resolved into sulphuric acid and sulphuric chloride: $2HClSO^3 = H^2SO^4 + Cl^2SO^2$.—By *pentachloride of phosphorus* it is converted into sulphuric chloride.—When poured into *water*, it sinks to the bottom, and gradually dissolves, with formation of sulphuric and hydrochloric acids. It has decidedly acid properties, and forms definite salts, in which its hydrogen is replaced by metals: thus it dissolves *chloride of sodium* at a gentle heat, with evolution of hydrochloric acid and formation of the salt $NaClSO^3$.—With *nitrate of sodium*, it yields sulphate of sodium and chloride of nitryl:

$$Na(NO^2)O + HClSO^3 = NaHSO^4 + NO^2Cl.$$

Ethyl- and phenyl-compounds analogous to sulphuric chlorhydrate are produced by the direct combination of ethylic and phenylic chloride with sulphuric oxide.—The *ethyl-compound*, $C^2H^5ClSO^3$, is a colourless, oily, pungent liquid, heavier than water, at the bottom of which it will lie for weeks without thoroughly decomposing. Sulphuric and hydrochloric acids may, however, be detected immediately after its immersion, and on neutralising the liquid with baryta, a soluble barium-salt is formed, probably the ethylsulphate.—A similar compound is formed by *chloride of methyl*, and apparently also by *chloride of acetyl*. (R. Williamson, Chem. Soc. Qu. J. x. 100.)

The *phenyl-compound*, $C^6H^5ClSO^3$, is a liquid which, when treated with excess of milk of lime, forms a soluble calcium-salt, $C^{12}H^8Ca''Cl^2S^2O^6$, which separates on evaporation in flat tabular crystals. (Hutchings, Chem. Soc. Qu. J. x. 102.)

Sulphuric Chloride, SO^2Cl^2. *Chloride of Sulphuryl. Sulphuric Chloraldehyde. Chlorosulphuric Acid.* (Regnault, Ann. Ch. Phys. [2], lxix. 170; lxxi. 445.—A. W. Williamson, Proc. Roy. Soc. vii. 11.)—This compound, which may be regarded as sulphuric acid in which 2 at. HO are replaced by 2 at. Cl, was discovered by Regnault, who first obtained it, mixed with chloride of ethylene, by passing dry chlorine into a mixture of ethylene-gas and sulphurous oxide; afterwards, in greater quantity, by exposing a mixture of chlorine and sulphurous oxide gases to strong sunshine for a considerable time. The resulting liquid may be freed from excess of chlorine by agitation with mercury and subsequent distillation. It is also produced by the action of phosphoric pentachloride on sulphuric oxide; but it is best obtained by distilling strong sulphuric acid with the pentachloride, or sulphate of lead with the oxychloride of phosphorus:

$$\begin{array}{rcrcl}
SO^3 & + & PCl^5 & = & SO^2Cl^2 + POCl^3 \\
H^2SO^4 & + & 2PCl^5 & = & SO^2Cl^2 + 2POCl^3 + 2HCl \\
3PbSO^4 & + & 2POCl^3 & = & 3SO^2Cl^2 + Pb^3P^2O^8
\end{array}$$

Sulphuric chloride is a colourless fuming liquid, of specific gravity 1·66. It boils at 77°, and may be distilled unchanged over caustic lime or baryta. When poured into water, it sinks in the form of oily drops, which gradually disappear, being converted into hydrochloric and sulphuric acids:

$$SO^2Cl^2 + 2H^2O = 2HCl + H^2SO^4.$$

With alcohol it behaves in a similar manner, thus:

$$SO^2Cl^2 + 2(C^2H^5)HO = 2C^2H^5Cl + H^2SO^4.$$

In the actual reaction, however, the sulphuric acid is converted into ethylsulphuric acid by the intervention of another atom of alcohol:

$$H^2SO^4 + (C^2H^5)HO = H^2O + (C^2H^5)HSO^4.$$

With dry ammonia-gas, or with commercial sesquicarbonate of ammonia, it forms sulphamide, according to Regnault:

$$SO^2Cl^2 + 4NH^3 = 2NH^4Cl + N^2H^4SO^2.$$

According to H. Rose, however, the product thus obtained is a mixture of sal-ammoniac and neutral sulphamate of ammonium (p. 476).

Nitrososulphuric Acid, $H^2SO^3(NO)^2$. *Nitrosulphuric Acid. Azotylsulphuric Acid. Nitrosulphurous Acid.*—A dibasic acid, known only in its alkaline salts, which are produced by the simultaneous action of sulphurous and nitric oxides on caustic alkaline solutions. (See Nitrososulphates, iv. 116.)

Sulphates of Nitrosyl or Azotyl.—These are salts produced by the action of sulphuric acid and sulphuric anhydride on the oxides of nitrogen. Three of them are known, corresponding exactly in composition to the sulphites of sodium, thus:

Sodium-salts.		Nitrosyl-salts.
$HNaSO^4$	Acid sulphate	$H(NO)SO^4$
Na^2SO^4	Neutral sulphate	$(NO)^2SO^4$
$Na^2S^2O^7$	Anhydrosulphate	$(NO)^2S^2O^7$.

Acid sulphate of nitrosyl was obtained by Weltzien (Ann. Ch. Pharm. cxv. 213; Jahresb. 1860, p. 106), as a white crystalline mass, by passing nitrous anhydride into normal sulphuric acid:

$$2H^2SO^4 + (NO)^2O = H^2O + 2H(NO)SO^4.$$

It is probably identical with the compound formed by heating the anhydrosulphate with sulphuric acid containing a little water, and crystallising:

$$(NO)^2S^2O^7 + H^2O = 2H(NO)SO^4.$$

Neutral sulphate of nitrosyl, $(NO)^2SO^4$, has been described by Gay-Lussac, Provostaye, Mitscherlich, and others. It is produced by the action of nitric peroxide on sulphuric acid, thus:

$$H^2SO^4 + 4NO^2 = (NO)^2SO^4 + 2HNO^3.$$

By this process, Gay-Lussac obtained it crystallised in four-sided prisms. It is also said to be produced by the action of nitric oxide on sulphuric acid (Henry and Plisson); by that of nitric peroxide on sulphurous acid (H. Davy); by dissolving the anhydrosulphate in a small quantity of hot oil of vitriol (Provostaye), and in other ways. (*Gmelin's Handbook*, ii. 447.)

The *anhydrosulphate of nitrosyl*, $(NO)^2S^2O^7 = (NO)^2SO^4.SO^3$, is formed by the action of sulphurous oxide on nitric peroxide (Provostaye), also of sulphuric ode on nitric oxide (Brüning); and by heating the compound $NO^2.SO^3$, resulting from the direct combination of nitric peroxide and sulphuric oxide (P. Weber)—(see p. 570). It is a hard, white, amorphous mass, which fuses when heated, and volatilises without decomposition. It dissolves in concentrated sulphuric acid, apparently without change; but with slightly diluted sulphuric acid, it forms a bulky crystalline substance, probably the acid sulphate of nitrosyl. When heated, it gives off brown vapours; and as the distillation is continued, the distillate approaches more and more to the composition $N^2O^3.3SO^3$, or $(NO)^2SO^4.2SO^3$. (Weber, Jahresb. 1862, p. 94.)

All the sulphates of nitrosyl are deliquescent, and are immediately decomposed by water into sulphuric acid and nitric oxide gas.

The crystals which form in the leaden chambers during the manufacture of oil of vitriol, when only an insufficient quantity of steam is admitted, are perhaps a mixture of the different sulphates of nitrosyl just noticed. According to Weber, however (*loc. cit.*), they consist entirely of the acid sulphate, $H(NO)SO^4$.

Metallic Sulphates.

General formula, M^2SO^4, or a multiple thereof.—The sulphates form a very abundant class of salts, which are usually obtained, as above mentioned, by the action of sulphuric acid on metals, or on their hydrates, oxides, and salts. Some of them are formed by the decomposition of other sulphates: *e.g.*, ferrous sulphate by the action of metallic iron on cupric sulphate, and the latter by the action of metallic copper on the sulphate of silver produced in the process of gold-refining (ii. 925). Insoluble sulphates (as those of barium and lead) are formed by precipitation, and the sulphates of potassium and sodium may be formed by fusing the insoluble sulphates of barium, strontium, calcium, and lead with potassic or sodic carbonate, or by boiling the insoluble sulphate with a solution of alkaline carbonate. Lastly, sulphates are formed by the oxidation of sulphides: the sulphates of iron, zinc, and copper are obtained in this manner, by oxidation of the native sulphides of those metals.

The sulphates may be divided into the following groups:—

1. Type, $H^2SO^4 = \left.\begin{matrix}(SO^2)''\\H^2\end{matrix}\right\}O^2$.—This group includes the sulphates of the monatomic metals and the neutral sulphates of the diatomic metals. With the alkali-metals, sulphuric acid forms acid and neutral salts: *e.g.*, $KHSO^4$ and K^2SO^4; also double salts,

such as $(NH^4)NaSO^4$. Potassium and sodium also form anhydrosulphates, composed of a molecule of the neutral salt united with sulphuric anhydride: *e.g.*, $NaSO^4.SO^3$. All the sulphates of the alkali-metals are soluble in water; the neutral potassium-salt, however, is much less soluble than any of the others.

The diatomic metals—that is to say, all the earth-metals excepting aluminium, thorinum, and zirconium, and the greater number of the heavy metals,—form neutral sulphates, represented by the general formula $M''SO^4$. The sulphates of barium, strontium, calcium, and lead are found native. The barium- and lead-salts are insoluble in water; the strontium-salt almost insoluble; the calcium-salt slightly soluble; the magnesium-salt and the heavy metal sulphates are freely soluble, except that of mercury, $Hg''SO^4$, which is decomposed by water. The heavy metal sulphates have an acid reaction, and all of them, except the sulphate of lead, and perhaps those of manganese and zinc, are decomposed by ignition.

2. *Sulphates formed on the Type of a Double Molecule of Sulphuric Acid*, $H^4S^2O^8 = \left.\begin{matrix}(\overset{\prime\prime}{S}O^2)^2\\ H^4\end{matrix}\right\}O^4$.—This group includes a few simple sulphates (e. g., stannic sulphate, $Sn^{iv}S^2O^8$, and zirconic sulphate, $Zr^{iv}S^2O^8$) and a large number of double sulphates, containing: (*a*), 1 atom of a diatomic and 2 atoms of a monatomic metal, such as potassio-cupric sulphate, $K^2Cu''S^2O^8$; (*β*), 1 atom of monatomic and 1 atom of triatomic metal, such as common alum, or potassio-aluminic sulphite, $KAl'''S^2O^8$. All these double sulphates are soluble salts, decomposible into their constituent salts by excess of water or by diffusion. The sub-group *a* likewise includes the acid sulphates of barium and calcium, $Ba''H^2S^2O^8$ and $Ca''H^2S^2O^8$.

3. Type, $H^6S^3O^{12} = \left.\begin{matrix}(\overset{\prime\prime}{S}O^2)^3\\ H^6\end{matrix}\right\}O^6$.— This group includes the neutral sulphates of the triatomic metals: *e.g.*, $\overset{\prime\prime\prime}{Al}{}^2S^3O^{12}$, $\overset{\prime\prime\prime}{Fe}{}^2S^3O^{12}$, &c. These salts are often found native: they are soluble, strongly acid compounds, decomposible by ignition. To the same group belong certain acid and double sulphates of the alkali-metals: *e.g.*, $K^4H^2S^3O^{12}$ and $K^4Li^2S^3O^{12}$.

There are also a few sulphates derived from higher multiples of H^2SO^4, which will be noticed further on.

Nearly all sulphates are crystallisable. The insoluble or difficultly soluble sulphates of lead, barium, strontium, and calcium occur native, in large well-defined crystals; many soluble sulphates also in smaller crystals, or crystalline masses. Many crystalline sulphates contain considerable quantities of water of crystallisation: thus the sulphates of iron, cobalt, nickel, manganese, zinc, and magnesium crystallise with 7 at. water; the double sulphates of the alkali-metals and the metals of the ferromagnesian group with 6 at. water; the alums with 12 at. water.

Among the crystalline sulphates, there are several isomorphous groups—viz., the anhydrous sulphates of potassium and sodium (trimetric); the anhydrous sulphates of calcium, strontium, barium, and lead (trimetric); the pentahydrated sulphates of manganese and copper (triclinic); the hexhydrated sulphates of zinc, nickel, and cobalt (monoclinic); the hexhydrated double sulphates of the alkali-metals with magnesium, zinc, nickel, cobalt, iron, manganese, and copper—*e.g.*, $K^2Mg''S^2O^8.6H^2O$ (monoclinic); and the alums, or dodecahydrated double sulphates of the alkali-metals with the sulphates of triatomic metals—*e.g.*, $KAl'''S^2O^8.12H^2O$ (monometric, and mostly octahedral).

The simple sulphates of the ferromagnesian family, with 5 or 7 at. water, retain 1 at. with very considerable force. Thus sulphate of magnesium, $MgSO^4.7H^2O$, loses 6 at. water at a temperature not much above 100°; but it holds back the seventh atom, even when heated to upwards of 200°. This last atom of water retained by the ferromagnesian sulphates was called, by Graham, constitutional water. The monohydrated sulphates of the form $M''SO^4.H^2O$ are analogous to glacial sulphuric acid, $H^2SO^4.H^2O$.

The dodecahydrated double sulphates of the alkali-metals and triatomic metals constitute the true alums. The sulphates of ammonium, potassium, and sodium are capable of forming alums with the aluminic, ferric, chromic, and manganic sulphates: the existence of sodium-iron-alum and sodium-manganese-alum appears, however, to be doubtful. Alums have also been formed containing the monatomic metals, thallium and silver: *e.g.*, silver-aluminium-alum, $AgAl'''S^2O^8.12H^2O$; and Wurtz has obtained an ethyl-ammonium-alum, $(C^2H^8N)Al'''S^2O^8.12H^2O$. In addition to these, there are several pseudo-alums, derived in like manner from 2 at. sulphuric acid, but having a different number of atoms of crystallisation-water, or a different crystalline form—*e.g.*, $KCr'''S^2O^8.6H^2O$; or containing diatomic metals, and derived from 4 at. sulphuric acid, such as $Mn''(Al''')^2S^4O^{16}.24H^2O$; $Fe''(Fe''')^2S^4O^{16}.24H^2O$, &c.

The genuine alums are all soluble in water, forming solutions which have a styptic taste, and marked acid reaction. The first effect of heat upon the alums is to drive off their water of crystallisation; a further degree of heat renders the dried residues very difficultly soluble in water, while a still higher temperature converts them into basic salts by the loss of sulphuric anhydride. The ammonium-alums, when heated, leave a residue of pure trioxide. The fixed alkali-alums leave a residue of trioxide mixed with sulphate of alkali-metal. It requires a very powerful and prolonged heat to drive off the last traces of sulphuric acid from the trioxides thus produced.

Basic Sulphates.—Most of the alums yield more or less defined basic salts. The best known of these is the native crystalline alum-stone, having the formula $KAlS^2O^8.Al^2O^3.4H^2O$. It corresponds in composition with the basic ammonium-alum formed by digesting gelatinous alumina in a hot solution of the normal alum, and having the formula $(NH^4)AlS^2O^8.\ Al^2O^3.\ 4H^2O$.

The diatomic metals yield a large number of basic sulphates, which may be regarded as normal sulphates, combined with metallic oxide replacing the water of hydrated sulphuric acid on its salts. Thus there is a dibasic sulphate of zinc, $Zn''SO^4.Zn''O$, corresponding to glacial sulphuric acid, $H^2SO^4.H^2O$; a tribasic sulphate of mercury, $Hg''SO^4.2Hg''O$, corresponding to the second hydrate of sulphuric acid, $H^2SO^4.2H^2O$; and a tribasic sulphate of copper, $Cu''SO^4.2Cu''O.3H^2O$, corresponding to blue vitriol, $Cu''SO^4.5H^2O$. Much more highly basic sulphates may also be obtained, and will be described in their places. Most of these basic sulphates are insoluble in water, and those few which are soluble are decomposed by a great excess of water into metallic oxide or hydrate and normal metallic sulphate.

Respecting the reactions of sulphates, see p. 536.

Sulphates of Aluminium.—*a*. The *normal* (or *neutral*) *sulphate*, $Al^2(SO^4)^3 = Al^2O^3.3SO^3$, occurs, as a hydrate containing 18 at. water, in delicate fibrous masses or crusts, in various localities: as at Bilin in Bohemia, on the volcanic island of Milo in the Grecian Archipelago, in the crater of the volcano of Pasto, at Copiapo in Chile, Adelaide in Australia, &c.; it is known mineralogically as *alunogen*, *hair-salt*, *feather alum*, and *halotrichite*. Hardness = 1·5 to 2. Specific gravity = 1·6 to 1·8. Lustre vitreous. Colour white, or tinged with yellow and red. Subtranslucent to subtransparent.

This salt is prepared on the large scale as concentrated alum, for use in dyeing instead of common alum, by treating pure clay with strong sulphuric acid. The clay, which must be as free as possible from iron, is heated to redness to render it porous, then finely ground, and mixed with half its weight of sulphuric acid of specific gravity 1·45, in a reverberatory furnace, the hearth of which has the form of a walled pan. The mixture is heated till the acid begins to volatilise; the mass is exposed to the air for several days, then treated with water; and the resulting solution of aluminic sulphate is freed from iron by careful precipitation with ferrocyanide of potassium. The solution thus purified is then evaporated to a syrup, and transferred to small leaden pans, in which it solidifies to a crystalline mass (Dumas). According to Hurier and Brunel (Pharm. Centr. 1852, p. 544), this salt may also be obtained [anhydrous] by heating ammonium-alum in iron cylinders, the sulphite of ammonium thereby evolved being received in water, and reconverted into sulphate by oxidation in the air. According to Persoz (Ann. Ch. Phys. [3], lvi. 102), a solution of alum, or of sulphate, nitrate, or chloride of aluminium, mixed with a large excess of boiling concentrated sulphuric acid, deposits the anhydrous sulphate as a white powder.

Neutral aluminic sulphate crystallises with difficulty in thin, flexible, nacreous laminæ, having a sweetish taste, soluble in 2 pts. of water, insoluble in alcohol. According to Persoz, the crystallisation is much facilitated by adding alcohol to the solution. The salt when heated melts in its water of crystallisation, swells up strongly, and leaves a white porous mass, consisting of the anhydrous sulphate, which dissolves very slowly in water, and when heated to redness leaves pure alumina.

β. Basic Salts.—*Dibasic aluminic sulphate*, $2Al^2O^3.3SO^3 = Al^2(SO^4)^3.Al^2O^3$, is obtained by heating a solution of the normal sulphate with alumina or with the following salt, filtering while hot, and evaporating to dryness at a gentle heat. It is a gummy mass, which is decomposed by water into the normal sulphate and the tribasic salt. (Maus, Pogg. Ann. xi. 80.)

The *tribasic sulphate*, $3Al^2O^3.SO^3.9H^2O$, or $Al^2(SO^4)^3.2Al^2O^3.9H^2O$, occurs native as *aluminite*, a white, opaque, earthy mineral, of specific gravity 1·70; it is also precipitated from the solution of the normal sulphate on addition of a small quantity of ammonia. It dissolves in hydrochloric acid, and at a red heat gives off sulphuric oxide, and leaves alumina.

The *tetrabasic salt*, $4Al^2O^3.3SO^3.36H^2O$ or $Al^2(SO^4)^3.3Al^2O^3.36H^2O$, is produced by digesting finely-divided calcic carbonate, for several days, in a cold solution of alum in excess. It is perceptibly crystalline, and very soluble in dilute acids, even in warm acetic acid.—The same salt is obtained by the action of zinc on a cold solution of normal aluminic sulphate. The action is very slow, even when electrolytically accelerated by placing the materials on a platinum-dish; but after a week, a transparent jelly is obtained, which, when separated by washing from zinc and excess of aluminic sulphate, and dried over oil of vitriol, solidifies in small transparent masses having a vitreous fracture. (Debray, Bull. Soc. Chim. [2], vii. 1.)

The *pentabasic salt*, $5Al^2O^3.3SO^3.20H^2O$, is obtained by gently boiling a solution of the normal salt with zinc in a platinum-dish. A granular precipitate is thereby formed, easy to wash, and soluble in dilute acids; it gives off its water at 100°. (Debray.)

γ. Double Salts of Aluminic Sulphate. Alums.—The formula of normal aluminic alum is $Al'''M(SO^4)^2.12H^2O$, M denoting a monatomic, and for the most part an alkali-metal. Their general characters have been already described (p. 579).

Ammonio-aluminic Sulphate, $Al(NH^4)SO^4.12H^2O$. *Ammonia-alum.*—This salt is prepared, like potash-alum, by adding sulphate or chloride of ammonium to a solution of aluminic sulphate. It is also found native as *tschermigite*, at Tschermig in Bohemia, in octahedrons and fibrous masses: hardness = 1 to 2; specific gravity = 1·56. According to Buignet (Jahresb. 1861, p. 15), the specific gravity of the artificially prepared crystals is 1·653. It is more soluble in water than potash-alum, 100 pts. of water dissolving 5·22 pts. of it at 0°, and 421·9 pts. at 100°. In other respects it bears the closest resemblance to potash-alum, and is used for the same purposes; in fact, the application of the alums as mordants, &c., depends upon the sulphate of aluminium which they contain, not on the alkaline sulphate. When heated to redness, it leaves anhydrous alumina, and when heated with alkalis, it gives off ammonia.—A *basic ammonia-alum*, analogous to basic potash-alum, is obtained by gradually adding ammonia to a boiling solution of the normal alum, but not to complete saturation.

Argento-aluminic sulphate, or *Silver-alum*, $AlAg(SO^4)^2.12H^2O$, is obtained by heating equivalent quantities of argentic and aluminic sulphate with a small quantity of water, in an oil-bath, till the argentic sulphate is completely dissolved. It crystallises in octahedrons, and is resolved by water into its component salts. (Church, Chem. News, ix. 155.)

Cæsio-aluminic sulphate, or *Cæsium-alum*, $AlCs(SO^4)^2.12H^2O$, crystallises in octahedrons, having a glassy lustre (Bunsen). 100 pts. of water at 17° dissolve 0·619 pt. of this salt; in hot water it dissolves as easily as potash-alum. (J. Redtenbacher, J. pr. Chem. xciv. 42.)

Potassio-aluminic sulphate, or *Potash-alum*, $AlK(SO^4)^2.12H^2O$.—This is the salt to which the name alum is most generally applied. It is obtained by adding sulphate or chloride of potassium to a solution of sulphate of aluminium. The sulphate of aluminium is sometimes prepared for this purpose from clay by the action of sulphuric acid in the manner already described, but more frequently by the calcination of aluminous schists, which are argillaceous rocks containing considerable quantities of sulphide of iron. The sulphide of iron is converted, by exposure to the air, into ferrous sulphate and free sulphuric acid:

$$2FeS^2 + O^7 + H^2O = Fe''SO^4 + H^2SO^4;$$

and the sulphuric acid, acting on the alumina contained in the clay, forms sulphate of aluminium. These aluminous schists are found in two different geological positions—viz., in the transition strata [alum-slate], in which position they are largely impregnated with bitumen; and in the lower tertiary strata, just above the chalk [alum-earth]. The latter are much less compact than the former; consequently their oxidation is easier, and sometimes takes place spontaneously. The greater part of the alum manufactured in England, France, and Germany is obtained from the aluminous schists.

The most extensive alum manufactory in Great Britain is at Hurlett, near Paisley. The next in magnitude is at Whitby, of whose state and processes an instructive account was published by Mr. Winter in the twenty-fifth volume of "Nicholson's Journal." The stratum of aluminous schist is about twenty-nine miles in width, and is covered by strata of alluvial soil, sandstone, ironstone, shell, and clay. The alum-schist is generally found disposed in horizontal laminæ. The upper part of the rock is the most abundant in sulphur, so that a cubic yard taken from the top of the stratum is five times more valuable than the same bulk 100 feet below.

If a quantity of the schist be laid in a heap, and moistened with sea-water, it will take fire spontaneously, and continue to burn till the whole inflammable matter is consumed. Its colour is bluish-grey. Specific gravity = 2·48. It imparts a bituminous principle to alcohol.

The rock, broken into small pieces, is laid on a horizontal bed of fuel, composed of brushwood, &c. When about four feet in height of the rock is piled on, fire is set to the bottom, and fresh rock continually poured upon the pile. This is continued until the calcined heap is raised to the height of 90 or 100 feet. Its horizontal area is at the same time progressively extended, till it forms a great bed nearly 200 feet square, having about 100,000 yards of solid measurement. The rapidity of the combustion is allayed by plastering up the crevices with small schist moistened. Notwithstanding this precaution, a great deal of sulphuric or sulphurous acid is dissipated. 130 tons of calcined schist produce, on an average, one ton of alum. This result has been deduced from an average of 150,000 tons.

The calcined mineral is digested with water in pits usually containing about 60 cubic yards. The liquid is drawn off into cisterns, and afterwards pumped up again upon fresh calcined *mine.* This is repeated until the specific gravity becomes 1·15. The half-exhausted schist is then covered with water to take up the whole soluble matter. The strong liquor is drawn off into settling cisterns, where the sulphate of lime, iron, and earth are deposited. At some works the liquid is boiled, which aids its purification. It is then run into leaden pans 10 feet long, 4 feet 9 inches wide, 2 feet 2 inches deep at the one end, and 2 feet 8 inches at the other. This slope facilitates the emptying of the pans. Here the liquor is concentrated at the boiling heat. Every morning the pans are emptied into a settling cistern, and a solution of chloride of potassium (either pretty pure from the manufacturer, or crude and compound from the soap-boiler) is added. The quantity of chloride necessary is determined by a previous experiment in a basin, and is regulated for the workmen by the hydrometer. By this addition, the pan-liquor, which had acquired a specific gravity of 1·4 or 1·5, is reduced to 1·35. After being allowed to settle for two hours, it is run off into the coolers to be crystallised. At a greater specific gravity than 1·35, the liquor, instead of crystallising, would, on cooling, solidify in a magma resembling grease. Urine is occasionally added, to bring it down to the proper density.

After standing four days, the mother-waters are drained off, to be pumped into the pans on the succeeding day. The crystals of alum are washed in a tub and drained. They are then put into a lead pan, with as much water as will make a saturated solution at the boiling-point. Whenever this is effected, the solution is run off into casks. At the end of ten or sixteen days, the casks are unhooped and taken asunder. The alum is found exteriorly in a solid cake, but in the interior cavity in large pyramidal crystals, consisting of octahedrons, inserted successively into one another. This last process is called "roching." Mr. Winter says that 22 tons of chloride of potassium will produce 100 tons of alum, to which 31 tons of the black ashes of the soap-boiler, or 73 of kelp, are equivalent. Where much iron exists in the alum-ore, the alkaline chloride, by its decomposition, gives rise to an uncrystallisable chloride of iron. For this reason it is preferable to the sulphate of potassium.

Alum may also be obtained from cryolite, $Al^2F^6.3NaF$, by heating the mineral with three times its weight of strong sulphuric acid, whereby anhydrous neutral sulphate of aluminium and acid sulphate of sodium are obtained; treating the resulting mass with a small quantity of cold water to remove the acid sodium-salt; then digesting the anhydrous sulphate of aluminium with warm water, to convert it into the hydrated salt, and adding the proper quantity of sulphate of potassium. The alum thus obtained is nearly if not quite free from iron. (Persoz, Ann. Ch. Phys. [3] lvi. 105.)

At Tolfa near Rome, and in two or three other localities, there is found a mineral called *alunite* or *alum-stone*, consisting of common alum together with normal hydrate of aluminium, $AlK(SO^4)^2.2AlH^3O^3$. Now when this mineral is calcined, at a moderate heat, the hydrate of aluminium is decomposed into water and anhydrous alumina, while the sulphate of aluminium and potassium remains unaltered, provided the heat has been prevented from rising too high; and on treating the calcined mass with water, the double sulphate dissolves, while the alumina remains behind. The mineral before calcination is quite insoluble in water. The solution when evaporated yields the alum in cubic crystals, generally having a reddish tint produced by ferric oxide. This kind of alum, called *Roman alum,* is much valued by dyers, because the iron which it contains is in an insoluble state, and therefore cannot exert any injurious effect on the colours.—Alum prepared in the ordinary way always contains iron in the soluble state, viz. as ferric sulphate, $Fe^2(SO^4)^3$, which, being isomorphous with sulphate of aluminium, is difficult to remove by successive crystallisation. It may be precipitated by ferrocyanide of potassium, as described in the preparation of sulphate of aluminium; but a cheaper way, recommended by Thénard, is to dissolve the alum in boiling water, and stir the solution briskly with rods as it cools. The salt is thus reduced to a fine granular powder, which, when washed two or three times with cold water, yields alum containing only a trace of iron. [On the manufacture of alum, see further *Ure's Dictionary of Arts,* &c. i. 101—118.]

Alum sometimes occurs in nature ready-formed. This is the case at Pozzuoli near Naples, where it effloresces on the surface of the soil. It is dissolved out by water, and crystallised by evaporation.

Alum generally crystallises in regular octahedrons and in cubes. Its specific gravity is 1·7. The octahedral crystals are the most common, and are always deposited from boiling concentrated solutions. The cubic crystals have an especial tendency to form in solutions containing an excess of alumina, and at a temperature not exceeding 50°, as in the preparation of Roman alum. If carbonate of potassium be added to a solution of octahedral alum in water at 40° or 45°, till the precipitate ceases to redissolve completely, and the filtered liquor be then left to itself at a gentle heat, cubic alum will be obtained quite free from iron. On the other hand, when a solution of cubic alum in cold water is abandoned to spontaneous evaporation, the alum is deposited in octahedrons. The two forms are identical in composition (**Löwel**, Compt. rend. xxxvi. 595). Sometimes intermediate forms occur, like *figs.* 194, 195, 196 (CRYSTALLOGRAPHY, ii. 129), or combinations of the cube and octahedron with other forms of the monometric system, like *figs.* 199, 202, 204, 205, 208, 209, 212, 273 (ii. 130–132); also aggregates and distorted forms, like *figs.* 316, 317, 347, 348, &c. (ii. 159, 164).

According to Poggiale, 100 pts. of water dissolve 3·29 pts. of crystallised alum at 0°; 9·52 pts. at 10°; 22 pts. at 30°; 31 pts. at 60°; 90 pts. at 70°, and 357 pts. at 100° (*Graham's Elements*, 2nd edition, i. 607). The solution has a sweet and strongly astringent taste, an acid reaction, and dissolves zinc and iron, with evolution of hydrogen.—When 2 pts. of alum are dissolved in 1 pt. of boiling water, and the solution is left to cool in a closed vessel, no crystallisation takes place; but as soon as the vessel is opened, small octahedral crystals begin to form on the surface, and in a short time the crystallisation extends through the whole mass. This is an instance of supersaturation similar to that exhibited by sulphate of sodium. (**Löwel**, Ann. Ch. Phys. [3], xiii. 405.)

Crystallised alum effloresces slightly on exposure to the air. According to **Hertwig** (Pogg. Ann. lv. 99), it gives off 5 at. water at 100°, and 4½ at. more at 120°, leaving a residue containing $2AlK(SO^4)^2.5H^2O$. This residue evolved 4 at. water at 180°, leaving $2AlK(SO^4)^2.H^2O$; and at 200°, half of this remaining quantity is given off, leaving $4Al^2K(SO^4)^3 + H^2O$. According to **Gerhardt** (J. Pharm. [2], xii. 57) crystallised alum gives off 10 at. water at 120°, leaving a residue easily soluble in water; and at 200°, the whole is expelled, and the remaining anhydrous alum, sometimes called *burnt alum*, is insoluble. Alum heated to redness with charcoal in a close vessel yields a mixture called *Homberg's pyrophorus*, which becomes red-hot on exposure to the air. It consists of very finely-divided charcoal and sulphide of potassium, intermixed with sulphate of aluminium.

Alum is used in large quantities in many manufactures, especially in dyeing as a mordant. When added to tallow, it renders that substance harder. Printers' cushions and the blocks used in the calico-manufactory are rubbed with burnt alum, to remove any greasiness that might prevent the ink or colour from sticking. Wood sufficiently soaked in a solution of alum does not easily take fire, and the same is true of paper impregnated with it, which is moreover fitter for keeping gunpowder, as it excludes moisture. Paper impregnated with alum is also useful in whitening silver and silvering brass without heat. Alum mixed with milk facilitates the separation of the butter. Alum is also used in tanning. In medicine it is employed as an astringent.—On this addition of alum to bread, see i. 658.

Basic Alum, $\left.\begin{matrix}K^2O\\3Al^2O^3\end{matrix}\right\}4SO^3 = AlK(SO^4)^2.Al^2O^3$.—This compound occurs native with different proportions of water, as *Alunite* and *Löwigite*.

Alunite or *Alum-stone*, $AlK(SO^4)^2.Al^2O^3.3H^2O = AlK(SO^4)^2.2AlH^3O^3$,* is found chiefly in volcanic districts, as at Tolfa near Civita Vecchia, at the Solfatara near Naples, and at Puy de Garcy in Auvergne. It occurs in rhombohedral crystals, having the angle R : R = 89° 10′; oR : R = 124° 40′, and length of principal axis = 1·2523. Observed planes R, oR, $\frac{6}{7}$R, $\frac{1}{84}$R, − $\frac{6}{5}$R, and − 2R (**Breithaupt**). Cleavage nearly perfect parallel to the base, indistinct parallel to R. It also occurs massive, with a granular or impalpable texture. Hardness = 3·5 to 4. Specific gravity = 2·58 to 2·752. It has a vitreous lustre, white colour (sometimes greyish or reddish), and white streak. Transparent to subtranslucent. Fracture flat, conchoïdal, or uneven; of massive varieties splintery, sometimes earthy. Brittle. The crystals of this mineral are nearly pure; the massive varieties contain silica sometimes to the amount of 60 per cent. It is used for the preparation of Roman alum (p. 581).

A salt identical in composition with alunite is precipitated as a crystalline powder when a solution of alum is boiled with gelatinous alumina.

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* The formula given for this mineral at p. 161. vol. i., is incorrect.

Löwigite, $\begin{matrix}K^2O\\3Al^2O^3\end{matrix}4SO^3.9H^2O = 2[AlK(SO^4)^2.2AlH^3O^3].3H^2O$, occurs at Tolfa near Rome and at Taberze in Upper Silesia, in amorphous nodules having a perfectly crystalline fracture; hardness between 3 and 4; specific gravity = 2·58. At the temperature of boiling sulphur, it gives off 2·18 per cent. (= 1 at.) water, and at a slightly higher temperature 5·67 per cent. water together with sulphuric acid, leaving a residue, from which water extracts sulphate of potassium, but only small quantities of alumina. (F. Römer and Löwig, Jahresb. 1856, p. 877.—A. Mitscherlich, J. pr. Chem. lxxxiii. 474.)

A salt having the same composition is produced, with evolution of hydrogen, by the action of zinc on a solution of common alum. The action is slow, even in a warm solution, unless assisted by placing the zinc in contact with lead or platinum. By operating in a platinum capsule at 100°, the salt is readily obtained as a crystalline precipitate. Like alunite and löwigite, it is nearly insoluble in nitric and in hydrochloric acids, and can only be attacked by sulphuric acid diluted with an equal bulk of water. (Debray, Bull. Soc. Chim. [2], vii. 9.)

Rubidio-aluminic sulphate, or *Rubidium-alum*, $AlRb(SO^4)^2.12H^2O$, forms large, transparent, non-efflorescent, octahedral crystals, modified with faces of the cube and dodecahedron (Kirchhoff and Bunsen). 100 pts. of water at 17° dissolve 2·27 pts. of it; in hot water it dissolves as easily as potash-alum. (J. Redtenbacher, Jahresb. 1865, p. 704.)

Sodio-aluminic sulphate, or *Soda-alum*, $AlNa(SO^4)^2.12H^2O$, is found native, in fibrous crusts or masses, on the island of Milo in the Grecian Archipelago, at the Solfatara near Naples, and near Mendoza on the east of the Andes. It may be prepared artificially in the same manner as common potash-alum, and obtained in large splendid octahedrons, by leaving a solution of the component salts to evaporate spontaneously in a rather deep glass vessel, and covered with a layer of alcohol. It is much more soluble than potash-alum, 10 pts. of water at ordinary temperatures dissolving 11 pts. of it.

Thallio-aluminic sulphate, or *Thallium-alum*, $AlTl(SO^4)^2.12H^2O$, crystallises in regular octahedrons. (Lamy.)

Pseudo-alums containing Diatomic Metals.—*Ferroso-aluminic sulphate*, $\left.\begin{matrix}Al^2O^3\\Fe''O\end{matrix}\right\}4SO^3.24H^2O = \overset{\prime\prime\prime}{Al}{}^2Fe''(SO^4)^4.24H^2O$, is produced (according to Klauer) when a solution of the component salts, mixed with excess of sulphuric acid, is left to stand in a warm place, and crystallises after a few days in tufts of silky fibres.

The same salt occurs native, as *halotrichite* or *feather-alum* (in part), at Bodenmais and Morsfeld in Rhenish Bavaria, at Oroomiah in Persia (where it is used for making ink), and probably at Roseville, Richmond County, New York. It forms fibrous, silky, yellowish-white crystals, which become dull and pulverulent on exposure, and taste like common alum, but somewhat inky (Berthier, Rammelsberg, B. Silliman, Jun., *Dana's Minerology*, ii. 383).—The *hversalt* of Forchhammer, from Iceland, is an allied alum having the alumina partly replaced by ferric oxide, and the ferrous oxide by magnesia.—The *halotrichine* of Scacchi is a silky mineral from the Solfatara, containing $\left.\begin{matrix}2Al^2O^3\\3Fe''O\end{matrix}\right\}5SO^3.54H^2O$.

Ferroso-potassio-aluminic sulphate, $\left.\begin{matrix}Al^2O^3\\12Fe''O\\2K^2O\end{matrix}\right\}17SO^3.24H^2O$, remains in the earthy residue left on distilling the sulphurous soil of the crater of the Solfatara near Naples. It crystallises in bottle-green octahedrons, which are permanent in the air, and dissolve sparingly in water. (Dufrénay.)

Magnesio-aluminic sulphate, or *Magnesia-alum*, $Al^2Mg(SO^4)^4.24H^2O$, crystallises from a solution of the constituent salts containing a considerable excess of acid, in long needle-shaped crystals. It occurs native in similar crystals, as *feather-alum* or *pickeringite*. A specimen from Iquique in Peru was found by Hayes (Sill. Am. J. xlvi. 368) to contain 12·180 per cent. alumina, 4·682 magnesia, 36·322 sulphuric anhydride, and 45·450 water, besides 0·430 ferrous and manganous oxides, 0·126 lime, and 0·604 silica (= 99·744), agreeing nearly with the preceding formulæ. The magnesium is often replaced to a considerable extent by manganese, forming mangano-magnesian alum.

According to Klauer, a mixture of magnesic and aluminic sulphates containing free acid sometimes yields, by slow evaporation, warty groups of small prismatic crystals, containing $Al^2Mg^3(SO^4)^6.36H^2O$.

Manganoso-aluminic sulphate, or *Manganese-alum*, $Al^2Mn(SO^4)^4.24H^2O$, occurs, with the manganese more or less replaced by magnesium, in snow-white silky fibres, at

Lagoa Bay in South Africa (Apjohn, Phil. Mag. [3], xii. 103), near the Bosjeman river in South Africa (Stromeyer, Pogg. Ann. xxxi. 137), and near Lake Utah in North America (Smith, Sill. Am. J. [2], xviii. 372):

	SO^3.	Al^2O^3.	MnO.	MgO.	K^2O.	H^2O.	KCl.		
Lagoa Bay	33·51	10·65	6·60	0·36	. .	48·15	. .	=	99·27
Bosjeman river	36·77	11·51	1·95	3·69	. .	45·74	0·20	=	99·86
Lake Utah	38·85	10·40	2·12	3·94	0·20	46·00	. .	=	100·51

The deposit at Lagoa Bay is twenty feet thick, and is made up of fibrous crystals six inches long.

Sulphates of Ammonium.—*Acid*, $(NH^4)HSO^4$.—*Neutral*, $(NH^4)^2SO^4$.—Already described under AMMONIACAL SALTS (i. 193).

Ammonio-sodic sulphate, $(NH^4)NaSO^4.2H^2O$, crystallises from a mixture of sodic sulphate and ammonic chloride, or of ammonic sulphate and sodic chloride, either by slow evaporation, or from a solution concentrated by heat till a crystalline film forms on the surface. It is permanent in the air, gives off its crystallisation-water over oil of vitriol, and slowly recovers it on exposure to the air at 15° or 16°. Specific gravity of the crystallised salt = 1·63 at 15°; that of a solution of various strengths is as follows:

Percentage of crystallised salt	31·8	25·44	15·9	12·72	6·3
Specific gravity	1·1749	1·1380	1·0849	1·0679	1·0337

At a stronger heat, the dehydrated salt gives off ammonia, and leaves acid sulphate of sodium. (Schiff, Ann. Ch. Pharm. cxiv. 68.)

Sulphates of Antimony.—*Neutral antimonious sulphate*, $\overset{\prime\prime}{Sb}{}^2(SO^4)^3$, formed by boiling antimony with strong sulphuric acid, is a white saline mass, which is resolved by water into an insoluble basic and a soluble acid salt. According to Brandes, the salt crystallises, from solution in excess of sulphuric acid, in small needles.

Several basic sulphates of antimony are known.—A *sesquibasic salt*, $Sb^2O^3.2SO^3 = Sb^2O^3.2Sb^2(SO^4)^3$, is produced, according to Péligot, in small shining crystals, by treating oxychloride of antimony (algaroth-powder) with fuming sulphuric acid.—The *tribasic salt*, $Sb^2O^3.SO^3 = 2Sb^2O^3.Sb^2(SO^4)^3$, is obtained by digesting the preceding salt in the pulverised state with alcohol, and remains as a white powder on filtration (Brandes).—The *hexbasic salt*, $2Sb^2O^3.SO^3 = 5Sb^2O^3.Sb^2(SO^4)^3$, is formed from the sesquibasic salt by boiling with water.

An *acid antimonious sulphate*, $Sb^2O^3.4SO^3 = Sb^2(SO^4)^3.SO^3$, is formed, with evolution of hydrochloric acid, by treating powder of algaroth with strong sulphuric acid. It crystallises in needles, which, however, cannot be obtained in the dry state, except by keeping them for a long time in a vacuum on a plate of baked pipe-clay. (Péligot.)

Sulphates of Barium.—The *neutral sulphate*, $Ba''SO^4$, occurs very abundantly in nature as *Heavy spar* or *Barytes*, sometimes in crystals belonging to the trimetric system, sometimes massive (see HEAVY SPAR, iii. 137). It may be obtained as a crystalline powder by fusing 12 grms. of potassic sulphate with 52 grms. anhydrous chloride of barium in a well-closed crucible, and dissolving out the soluble salts with water. The crystals thus obtained agree in form and specific gravity with native heavy spar. (Manross, Ann. Ch. Pharm. lxxxii. 348; Jahresb. 1852, p. 9.)

By precipitating the solution of a barium-salt with sulphuric acid or a soluble sulphate, sulphate of barium is obtained, as a heavy, white, amorphous powder, of specific gravity 4·02—4·51 (Schröder, Jahresb. 1859, p. 12), insoluble in water, very slightly soluble in dilute acids, somewhat more soluble in strong sulphuric, nitric, and hydrochloric acids (ii. 503). It dissolves also to a perceptible extent in aqueous nitrate of ammonium, especially when the boiling solutions of a sulphate and a barium-salt, previously mixed with a little nitrate of ammonium, are poured alternately into a boiling solution of the same salt (Mittenzwei, J. pr. Chem. lxxv. 214). According to Scheerer (*ibid.* p. 113), the precipitation of sulphuric acid by barium-salts is retarded by the presence of metaphosphoric acid, but not of pyrophosphoric or orthophosphoric acid.

Sulphate of barium boiled with a concentrated solution of a fixed alkaline carbonate is decomposed, but never completely, into alkaline sulphate and barium-carbonate; a somewhat more complete decomposition is obtained by fusion with alkaline carbonates. Sulphate of barium is reduced to sulphide by ignition with charcoal or organic matter; also, according to Wurtz, by ignition in a stream of coal gas; or, according to Deville, in a stream of hydrogen mixed with vapour of carbonic disulphide.

Native sulphate of barium, in the state of powder and mixed with white lead, is used as a pigment; alone it has not sufficient body; the amorphous sulphate is prepared on the large scale by precipitation, and forms the pigment called **permanent**

The *acid salt*, $\mathrm{Ba''H^2(SO^4)^2}$, is produced (according to Berzelius) by pouring strong sulphuric acid on the ignited neutral sulphate, and leaving it to stand in a closed vessel in a warm place. According to Liès-Bodart and Jacquemin (J. pr. Chem. lxxv. 314), strong sulphuric acid dissolves oxide, chloride, sulphide, chlorate, phosphate, &c. of barium, forming acid sulphate of barium, which crystallises in microscopic prisms; and if the mother-liquor be left in an open vessel, so that it may slowly absorb moisture, it deposits silky needles containing $\mathrm{Ba''H^2(SO^4)^2.2H^2O}$. Both the anhydrous and the hydrated crystals are immediately decomposed by water.

Bario-sodic sulphate, $\mathrm{Ba''Na^2(SO^4)^2}$, is produced (according to Berthier) by fusing its constituent salts together in equivalent quantities, and forms on cooling an opaque very hard mass, having a pearly lustre.

Sulphates of Bismuth.—When bismuth is heated with strong sulphuric acid, sulphurous oxide is evolved, and the metal is converted into a white insoluble powder, consisting of the *normal sulphate*, $\overset{\prime\prime\prime}{\mathrm{Bi}}\mathrm{{}^2O^3.3SO^3}$ or $\overset{\prime\prime\prime}{\mathrm{Bi}}\mathrm{{}^2(SO^4)^3}$, which is decomposed by water, yielding a very acid salt, which dissolves; and a *tribasic sulphate*, $\mathrm{Bi^2O^3.SO^3.H^2O}$, or $\mathrm{2Bi^2O^3.Bi^2(SO^4)^3.3H^2O}$, which remains.—There is also a *sesquibasic sulphate*, $\mathrm{Bi^2O^3.2SO^3.3H^2O}$, or $\mathrm{Bi^2O^3.2Bi^2.(SO^4)^3.9H^2O}$, which is obtained in small delicate needles, when an acid solution of nitrate of bismuth is mixed with sulphuric acid. (Heintz.)

Bismutho-potassic sulphate, $\mathrm{Bi'''K^3(SO^4)^3}$, is precipitated on dropping an acid solution of bismuth-nitrate into a concentrated solution of potassic sulphate, the latter not being in excess. The white pulverulent precipitate must be dried on a porous tile in the exsiccator. It is decomposed by water. If a dilute solution of potassic sulphate be used, the precipitate has the composition $\overset{\prime\prime\prime}{\mathrm{Bi}}\mathrm{{}^2K^4(SO^4)^5}$. (Heintz.)

Sulphates of Cadmium.—The *neutral salt*, $\mathrm{Cd''SO^4}$, forms (according to Stromeyer) efflorescent crystals containing 4 at. water. According to Kühn and v. Hauer (J. pr. Chem. lxiv. 477; Chem. Soc. Qu. J. viii. 250), an acid solution of the salt, concentrated at the boiling heat, deposits nodular crystals, which contain $\mathrm{Cd''SO^4.H^2O}$, and give off their water at 100°; their specific gravity is 2·939 (Buignet, Jahresb. 1861, p. 15). The crystals formed at ordinary temperatures contain $\mathrm{3Cd''SO^4.8H^2O}$, give off nearly 3 at. water at 100°, and the rest at a low red heat (v. Hauer); their specific gravity is 3·05 (Gieseke, Jahresb. 1860, p. 17). According to Rammelsberg (Pogg. Ann. cxv. 579), they are isomorphous with the sulphates of didymium and yttrium containing corresponding quantities of water. W. Delffs (Pharm. Centr. 1854, p. 380) recommends sulphate of cadmium as a distinguishing test between several organic acids, inasmuch as it forms precipitates with oxalates, mellitates, citrates, cuminates, and cinnamates at ordinary temperatures,—with tartrates, racemates, fumarates, and suberates only when heated,—and does not precipitate the aconitates, malates, succinates, benzoates, or salicylates under any circumstances.

Ammoniacal cadmic sulphate, $\mathrm{Cd''SO^4.6NH^3}$, or *Sulphate of tetrammonio-cadmio-diammonium*, $\mathrm{N^2[H^2(NH^4)^4Cd'']SO^4}$, is formed, as a white powder, when anhydrous cadmic sulphate is allowed to absorb ammonia-gas till it is saturated. (H. Rose.)

Ammonio-cadmic sulphate, $\mathrm{Cd''(NH^4)^2(SO^4)^2.6H^2O}$, separates in monoclinic crystals, from a solution containing equivalent quantities of the component salts.—The corresponding *potassium-salt*, which is isomorphous with it, is not so easily formed, inasmuch as the solution is apt to deposit sulphate of potassium; it is efflorescent.—The *magnesium-salt*, $\mathrm{Cd''Mg''(SO^4)^2.6H^2O}$, crystallises from dilute sulphuric acid, half saturated with cadmic, and half with magnesic carbonate, in easily soluble four-sided prisms.—The *sodium-salt*, $\mathrm{Cd''Na^2(SO^4)^2.6H^2O}$, separates from concentrated solution in small nodules. (v. Hauer.)

Sulphate of Cæsium. See Cæsium (i. 1115).

Sulphates of Calcium.—The *neutral sulphate*, $\mathrm{Ca''SO^4}$, occurs native, both in the anhydrous state as anhydrite (i. 295), and as a hydrate, $\mathrm{Ca''SO^4.2H^2O}$, forming gypsum and its several varieties (ii. 962). The anhydrous sulphate may be obtained in crystals having the form and specific gravity (2·9) of anhydrite, by fusing potassic sulphate with excess of calcic chloride (Manross, Jahresb. 1852, p. 9; see also Simmler, *ibid.* 1859, p. 132). The hydrated salt is formed by precipitating a solution of calcic chloride with a soluble sulphate or dilute sulphuric acid. It is very slightly soluble in water, the anhydrous salt nearly insoluble. According to Lassaigne, 1 pt. of the hydrate dissolves in 332 pts. of water at any temperature; but according to Poggiale, the solubility is greatest at 35°, 1 pt. of the salt dissolving at that temperature in 393 pts. water, at 0° in 488 pts., and at 100° in 460 pts. Water containing hydrochloric or nitric acid dissolves it in larger quantity, in consequence of partial decomposition; the solubility is likewise increased by the presence of common salt;

hence the occurrence of gypsum in salt-springs. Calcic sulphate dissolves also in excess of a saturated solution of sodic hyposulphite, with moderate facility at ordinary temperatures, more quickly on warming, being at the same time converted into calcic hyposulphite, which unites with the excess of sodic hyposulphite, forming a soluble double salt; and on adding alcohol to the solution, this double salt is precipitated as a heavy oily liquid, which solidifies in needle-shaped crystals. The solubility of calcic sulphate in sodic hyposulphite affords a means of separating it from baric sulphate. (Diehl, J. pr. Chem. lxxix. 430.)

Gypsum heated to 100° or 120° gives off three-fourths of its water somewhat quickly, but the last fourth is not expelled below 200°—250°. The hydrated calcic sulphate deposited in steam-boilers has the same composition as gypsum dried at 100°, viz. $2CaSO^4.H^2O$, and a specific gravity of 2·7. Dehydrated gypsum melts at a red heat without decomposition, and on cooling assumes the crystalline structure of anhydrite. When gypsum dehydrated at a moderately high temperature, and pulverised, is agitated with water, it takes up 2 at. water, and solidifies to a very hard mass, the solidification being quicker in proportion as the gypsum has been dehydrated at a lower temperature; if this temperature exceeds a certain limit, the gypsum bakes together, and is then incapable of taking water. The hydrated gypsum expands in solidifying, so that it easily fills the cavities of any mould in which it is cast: hence the use of gypsum or plaster of Paris in taking casts (ii. 962). Calcic sulphate ignited with charcoal or organic matter is reduced to sulphide.

Acid sulphate of calcium, or *Calcio-hydric sulphate*, $Ca''H^2(SO^4)^2$, is produced, (according to Berzelius) by digesting the anhydrous neutral salt with sulphuric acid at 80°—100°. It forms a granular mass, the particles of which appear under the microscope as short, colourless, transparent prisms. It absorbs moisture from the air, and is then quickly decomposed into sulphuric acid and the neutral sulphate.

Calcio-sodic sulphate, $Ca''Na^2(SO^4)^2$, occurs native as glauberite or brongniartin (ii. 845), in transparent rhombic prisms. According to Berthier, it may be obtained in the same form by fusing a mixture of calcic and sodic sulphates. When 50 pts. of sodic sulphate are heated with 25 pts. water in which 1 pt. of gypsum has been stirred up, the liquid deposits at 80° a pulp of crystalline needles, consisting of the salt $Ca''Na^4(SO^4)^3.2H^2O$. At a higher temperature, these needles are converted into microscopic, rhombohedral, anhydrous crystals of glauberite, $Ca''Na^2(SO^4)^2$. The latter is also formed immediately, if twice the above quantity of water is used at the beginning of the process, and the liquid heated to boiling. These artificial crystals of glauberite are transparent, like the native crystals from Villarubia, but become opaque and much more friable by ignition.

Sulphate of calcium likewise unites by fusion with the fluorides of barium, strontium, and calcium, forming clear fluid masses, which become milk-white on solidifying.

Sulphates of Cerium.—α. *Ceric Salts. Neutral* or *normal Ceric sulphate*, $Ce^2(SO^4)^3 = Ce^2O^3.3SO^3$, obtained by dissolving ceric oxide in sulphuric acid and evaporating, forms efflorescent crystals belonging to the hexagonal system, which dissolve in a small quantity of water, but are decomposed by a larger quantity, with precipitation of a basic salt requiring 2,500 pts. of water to dissolve it (Mosander). On dissolving this basic salt in sulphuric acid, the neutral salt crystallises out again with 9 at. water (Hermann, J. pr. Chem. xxx. 184).—The *basic salt* contains, according to Hermann, $3Ce^2O^3.4SO^3.9H^2O$, or $4Ce^2(SO^4)^3.5Ce^2O^3.27H^2O$. Marignac regards it as a ceroso-ceric salt. A basic ceric sulphate, the composition of which is not given, is prepared, according to Holzmann (J. pr. Chem. lxxv. 321; Jahresb. 1858, p. 132), by dissolving the brown powder obtained by roasting a mixture of cerous oxalate and *magnesia alba* (i. 832) in boiling nitric acid, heating the solution till nearly all the free nitric acid is expelled, triturating 100 grms. of the crystalline mass which forms on cooling with 100 cub. cent. of water, and adding the quickly filtered solution to 2 litres of boiling water previously mixed with 12 cub. cent. of sulphuric acid. The basic ceric sulphate which then separates is to be washed by decantation with water containing the same quantity of sulphuric acid.

Potassio-ceric sulphate, $\overset{'''}{Ce}{}^2K^4(SO^4)^5 = \left.\begin{matrix}Ce^2O^3\\2K^2O\end{matrix}\right\}5SO^3$, is obtained, by immersing crystallised potassic sulphate in a solution of ceric sulphate, as a lemon-yellow powder, which dissolves in water and crystallises therefrom, but is insoluble in a saturated solution of potassic sulphate. When ignited it turns white, gives off sulphuric oxide and oxygen, and leaves ceroso-potassic sulphate (Hermann).—*Ammonio-cerous sulphate* forms monoclinic crystals.

β. *Cerous Salts.*—*Neutral cerous sulphate*, $Ce''SO^4.3H^2O$, is obtained by dissolving cerous carbonate in sulphuric acid, or (according to Marignac) by dissolving ceroso-ceric sulphate in water acidulated with sulphuric or nitric acid, diluting the yellowish-red solution with water, and boiling the insoluble salt, which separates after washing, with sulphuric or hydrochloric acid, till it dissolves, and forms a perfectly colourless solution. This solution, when evaporated, yields cerous sulphate in colourless rhombic octahedrons (sometimes reddish from the presence of didymium). According to Otto, they contain 3 at. water, which is expelled by heat. They dissolve with moderate facility in cold water, and the solution, when heated, deposits reddish prisms of a much less soluble salt, containing $2CeSO^4.3H^2O$; they must be taken out of the hot liquid and pressed, as if the mother-liquor is left to cool upon them, they redissolve (Otto). According to Hermann (J. pr. Chem. xcii. 113; Jahresb. 1864, p. 194), four other hydrates—containing respectively $3CeSO^4.5H^2O$, $CeSO^4.2H^2O$, $3CeSO^4.8H^2O$, and $CeSO^4.3H^2O$, separate from moderately warm solutions of cerous sulphate, under apparently similar circumstances, and cannot be obtained at pleasure. They all crystallise in rhombic forms, and appear to be homœomorphous. The $\frac{8}{3}$-hydrate is the most frequent, separating both on warming and by slow evaporation, in short prisms, which retain their lustre on exposure to the air.

Ammonio-cerous sulphate separates, on boiling a solution of its component salts, as a crystalline powder, which, by solution and recrystallisation, may be obtained in obtuse rhombohedrons.

Potassio-cerous sulphate, $Ce''K^2(SO^4)^2$, separates as a white powder, on immersing solid potassic sulphate in a solution of cerous sulphate which may contain free acid. It is insoluble in a saturated solution of potassic sulphate, but dissolves slightly in pure water, and crystallises on cooling from solution in boiling water. The formation of this salt affords a means of separating cerium from most other metals (i. 833). It melts without decomposition when heated (Berzelius).—Another *potassio-cerous sulphate*, $\overset{\prime\prime\prime}{Ce}{}^2K^2(SO^4)^3$, separates (according to Hermann) as a white powder, on mixing the concentrated solutions of equal weights of potassic and cerous sulphates.

Sodio-cerous sulphate, $\overset{\prime\prime\prime}{Ce}{}^2Na^2(SO^4)^3$, analogous to the potassium-salt last-mentioned, separates as a white granular precipitate, on heating a mixed solution of the component salts to the boiling-point. (Beringer.)

γ. *Ceroso-ceric Salts.*—The salt $3CeO.2Ce^2O^3.4SO^3.H^2O$ is formed, according to Marignac, as a yellow mass, by treating ignited ceric oxide with sulphuric acid. It dissolves easily in water strongly acidulated with sulphuric or nitric acid, and is reduced to cerous sulphate by boiling with nitric or hydrochloric acid. According to Rammelsberg (Pogg. Ann. cviii. 40; Jahresb. 1859, p. 136), the yellowish-red solution of ceroso-ceric oxide in sulphuric acid yields, by slow evaporation, first brown-red hexagonal crystals of a salt, *A*, containing $\overset{\prime\prime\prime}{Ce}{}^2\overset{\prime\prime}{Ce}{}^3(SO^4)^6.18H^2O = 3Ce''SO^4.\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^3.18H^2O$, which are decomposed by water, with separation of a sulphur-yellow basic salt; afterwards a yellow indistinctly crystalline salt, *B*, containing $\overset{\prime\prime\prime}{Ce}{}^2Ce''(SO^4)^4.8H^2O$, or $Ce''.\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^4.8H^2O$, which is decomposed by water in the same manner as the former. The light-yellow precipitate, separated from either of these salts by water, contains $2Ce^3O^4.3SO^3.6H^2O$, and, as well as the salts *A* and *B* themselves, leaves, when strongly ignited, a residue of pure ceroso-ceric oxide (Rammelsberg). According to Hermann (Jahresb. 1864, p. 194), Rammelsberg's yellow-red salt *A* contains $2Ce''.SO^4.\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^3.27H^2O$, and his yellow salt *B* consists of $Ce''SO^4.\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^3.8H^2O$. Hermann supposes also that there are several other yellow ceroso-ceric sulphates. The composition of basic *ceroso-ceric sulphate* likewise varies, according to Hermann, with its mode of preparation.

A solution of the salt *A* yields, on addition of potassic sulphate, a yellow crystalline precipitate, varying in composition according to the proportions in which the two salts are mixed, and the temperature and concentration of the solutions, but generally consisting of a mixture of at least two compounds—viz., $3K^2SO^4.3Ce''SO^4.\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^3.6H^2O$ and $6K^2SO^4.3Ce''SO^4.\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^3.6H^2O$. Rammelsberg is, however, of opinion that the composition of these salts may be more correctly expressed by regarding the cerous oxide and potash as bases which replace one another isomorphously. Marignac (Ann. Min. [5] xv. 275) obtained, by spontaneous evaporation of a solution containing potassic and ceroso-ceric sulphates, small yellow crystals having the composition $Ce^3O^4.4SO^3 + 4(K^2O.SO^3) + 4H^2O$ or $4K^2SO^4.Ce''SO^4.\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^3.4H^2O$, and consisting of monoclinic combinations $+P . -P . oP . \infty P\infty . [\infty P\infty] . [\frac{1}{2}P\infty] . +\frac{1}{2}P\infty$, &c.; sometimes pyramidal, from predominance of $+P$ and $-P$; sometimes tabular, by predominance of oP. Angle $+P : +P$ (clinod.) $= 83° 7'$; $-P : -P$ (clinod.) $= 92° 23'$; $oP : \infty P\infty = 100° 40'$; $oP : +P = 104° 20'$; $oP : -P = 116° 20'$; $oP : [\frac{1}{2}P\infty] = 134° 10'$.

—*Ammonio-ceroso-ceric sulphates* are obtained in the same manner as the potassic salts Besides a crystallo-granular precipitate containing $4(NH^4)^2SO^4.2Ce''SO^4.\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^3.4H^2O$, large, orange-red, monoclinic crystals are formed, containing $9(NH^4)^2SO^4.Ce''SO^4.2\overset{\prime\prime\prime}{Ce}{}^2(SO^4)^3.12H^2O$, easily soluble in water, and leaving pure ceroso-ceric oxide when ignited (Rammelsberg). Marignac obtained an ammonio-ceroso-ceric salt, analogous in form and composition to his potassio-ceroso-ceric salt.

Sulphates of Chromium. (Schrötter, Pogg. Ann. liii. 513.—Traube, Ann. Ch. Pharm. lxvi. 87, 168.—Moberg, *ibid.* lxvi. 92.—Leykauf, J. pr. Chem. xix. 225. —Löwel, Ann. Ch. Phys. [3] xl. 42; xliv. 313; Jahresb. 1855, p. 376.)—*a. Chromic Salts.*—The *normal* or *neutral salt*, $\overset{\prime\prime\prime}{Cr}{}^2(SO^4)^3$ or $\overset{\prime\prime\prime}{Cr}{}^2O^3.3SO^3$, exhibits a violet and a green modification. The violet sulphate is obtained by leaving 8 pts. of chromic hydrate dried at 100°, and 8 or 10 pts. of strong sulphuric acid, in a loosely-stoppered bottle for several weeks. The solution, which is green at first, gradually becomes blue, and deposits a greenish-blue crystalline mass. On dissolving this substance in water, and adding alcohol, a violet-blue crystalline precipitate is formed; and by dissolving this precipitate in very weak alcohol, and leaving the solution to itself for some time, small regular octahedrons are deposited, containing $Cr^2(SO^4)^3.15H^2O$. Another mode of preparing it is to dissolve 5 pts. of chromic hydrate in 12½ pts. strong nitric acid; dilute the solution with 12½ pts. of water; and after boiling for a quarter of an hour, and leaving the liquid to cool (whereupon it turns red), add 7½ pts. strong sulphuric acid previously diluted with 15 pts. of water, and cooled. On shaking up this solution with 120 pts. of alcohol, the salt separates in small crystals, which must be washed with alcohol and dried between filter-paper. (Löwel, Ann. Ch. Phys. [3] xl. 42.)

The *green sulphate*, $\overset{\prime\prime\prime}{Cr}{}^2(SO^4)^3.5H^2O$, is prepared by dissolving chromic oxide in strong sulphuric acid at a temperature between 50° and 60°; also by boiling a solution of the violet sulphate; or by heating the crystals of the violet salt to 100°, whereupon they give up 10 at. water, and melt to a green liquid which solidifies to a green amorphous mass. The liquid, when quickly evaporated, yields a green non-crystalline salt having the same composition as the violet sulphate. The green sulphate dissolves readily in alcohol, forming a blue solution; but the violet salt is insoluble in alcohol. The solution of the green sulphate is not completely decomposed by soluble barium-salts at ordinary temperatures, a boiling heat being required to complete it; the violet sulphate, on the contrary, is deprived of all its sulphuric acid by barium-salts at ordinary temperatures. When either the green or the violet sulphate is heated to 190°, with excess of sulphuric acid, a light-yellow mass is obtained, which, when further heated, leaves a residue of anhydrous chromic sulphate, having a *red* colour. This anhydrous salt is completely insoluble in water, and dissolves with difficulty even in acid liquids.

Basic Salts.—The *sesquibasic sulphate*, $Cr^2O^3.2SO^3$, or $Cr^2O^3.2Cr^2(SO^4)^3$, is formed (according to Schrötter) when recently precipitated and still moist chromic hydrate is dissolved to complete saturation in moderately dilute sulphuric acid. The green solution thus formed leaves, on evaporation, a green residue, which appears dark ruby-red by transmitted light, is perfectly amorphous, and when heated to redness is converted, without change of colour, into chromic oxide. It dissolves readily in a small quantity of water; the solution exhibits a dark ruby colour by transmitted light, and on dilution with water, especially if heated, deposits a light-green powder.—The $\frac{9}{2}$-*basic salt*, $3Cr^2O^3.2SO^3.12H^2O = 7Cr^2O^3.2Cr^2(SO^4)^3.36H^2O$, is the light-green powder which separates on heating the dilute solution of the preceding salt (Schrötter).—The *dibasic salt*, $2Cr^2O^3.3SO^3 = Cr^2O^3.Cr^2(SO^4)^3$, is produced (according to Krüger) when a solution of chromic sulphate is heated till the original green colour changes to rose-red. It is insoluble in water.—The precipitates formed by alkalis in solutions of chromic sulphate are likewise basic salts, which however vary greatly in composition, according to the concentration of the liquid and the quantity of alkali added.

Double Salts of Chromic Sulphate. Chrome-alums.—*Ammonia-chrome-alum*, $Cr'''(NH^4)(SO^4)^2.12H^2O$, is prepared, like the corresponding potassium-salt, with sulphate of ammonium and chromic sulphate (Schrötter), or acid chromate of ammonium (Traute). It is less soluble than the potassium-salt, and crystallises more readily in splendid ruby-coloured octahedrons, which yield a lavender-blue powder. Specific gravity = 1·738. From a concentrated solution of violet chromic sulphate, it is precipitated, on addition of ammonium-sulphate, as a violet-blue crystalline powder. It is not precipitated from its aqueous solution by alcohol. The crystals effloresce slowly in contact with the air, and melt at 100°, with loss of 9 at. water, the residue slowly solidifying to a green gummy mass containing 3 at. water, which is the double salt corresponding to the green modification of chromic sulphate. At 200°, the other 3 at. water are given off, the green anhydrous salt then remaining.

The violet solution, prepared in the cold, passes at 75° into the green modification, and is then no longer crystallisable; if, however, it be left to itself for ten or twelve days after cooling, the violet colour is restored, and with it the capability of crystallisation.

Potassio-chromic Sulphate, or *Potassic Chrome-alum*, $\mathrm{Cr'''K(SO^4)^2.12H^2O}$.—This salt is produced: 1. By mixing the solutions of potassic chromate and violet chromic sulphate, adding a small quantity of sulphuric acid, and leaving the solution to evaporate.—2. By heating potassic dichromate with strong sulphuric acid:

$$\mathrm{K^2CrO^4.CrO^3 \ + \ 4H^2SO^4 \ = \ 2Cr'''K(SO^4)^2 \ + \ 4H^2O \ + \ O^2.}$$

The reduction of the chromic acid is, however, greatly facilitated by adding alcohol or other organic substance. Chrome-alum is, in fact, often obtained as a secondary product in the oxidation of organic bodies with sulphuric acid and potassic chromate, as in the preparation of valerianic acid from amylic alcohol. A very convenient mode of reduction also is to pass sulphuric oxide gas through the liquid. In this case only 1 at. sulphuric acid need be added, the reaction being represented by the equation:

$$\mathrm{K^2CrO^4.CrO^3 \ + \ H^2SO^4 \ + \ 3SO^2 \ = \ 2Cr'''K(SO^4)^2 \ + \ H^2O.}$$

Chrome-alum crystallises, by slow evaporation, in splendid octahedrons, sometimes very large and of a dark purple almost black colour: the smaller crystals exhibit, by transmitted light, a very fine ruby-red colour. The salt dissolves at ordinary temperature in 7 pts. of water. The solution has a dingy-blue colour, with a tinge of red, and when mixed with alcohol deposits the chrome-alum unaltered. When heated to 70° or 80°, it becomes green, perhaps from formation of green chromic sulphate or the corresponding modification of chrome-alum, which, like green chromic sulphate itself, is uncrystallisable. The green solution, if left at rest for some weeks, gradually recovers its violet colour, and then again yields crystals. The change of the purple into the green salt has sometimes been supposed to be attended with separation of the potassic and chromic sulphates; but, according to Schrötter and Löwel, it arises merely from loss of crystallisation-water. A solution of chrome-alum which has become green and uncrystallisable by heating, does not deposit any sulphate of potassium, even when concentrated; neither does that salt separate when the crystals are melted in a sealed tube; but the green liquid obtained by either of these processes yields, when heated in a dry atmosphere, a dark-green mass containing $\mathrm{CrK(SO^4)^2}$, with scarcely 3 at. water. The violet crystals containing $\mathrm{12H^2O}$, when left for several days in dry air, at a temperature between 25° and 30°, give off 6 at. water, and assume a lilac colour. At 100° another quantity of water goes off, and the crystals become green; and, by gradually raising the temperature to about 350°, the whole of the water may be expelled without causing the salt to melt. The anhydrous crystals are green, and dissolve without residue in boiling water, but at a temperature somewhat above 350°, they suddenly become greenish-yellow, without perceptible loss of weight, and are afterwards perfectly insoluble in water. (Löwel; see also Siewert, Ann. Ch. Pharm. cxxvi. 86; Jahresb. 1863, p. 223.)

Krüger, by precipitating a concentrated green solution of chrome-alum prepared at a high temperature, obtained a green viscid mass containing $\mathrm{Cr^2O^3.2SO^3 + K^2O.SO^3}$ or $\mathrm{\overset{'''}{Cr}{}^4K^6(SO^4)^9.Cr^2O^3}$. According to Otto, the aqueous solution of this salt, when left at rest for a very long time, is completely converted into violet crystals. Leykauf has proposed the use of the green mass for colouring oil-varnishes, caoutchouc, &c., and its solution as a green ink.

Sodio-chromic Sulphate, or *Sodic Chrome-alum*, $\mathrm{Cr'''Na(SO^4)^2.12H^2O}$.—Prepared by cautiously adding alcohol to a mixture of 1 at. acid chromate of sodium and 4 at. sulphuric acid. It is much more soluble than the corresponding ammonium- and potassium-salts, and cannot therefore be obtained in well-developed crystals. Under the exsiccator it separates as a violet warty mass. At 100° it gives off 8 at. water, leaving a green modification with 4 at. water. (Schrötter.)

Potassio-aluminio-chromic sulphate, $\mathrm{Cr'''Al'''K^2(SO^4)^4.24H^2O}$, and the corresponding *ammonium-salt*, are prepared by mixing the solutions of equivalent quantities of the alumina- and chrome-alums, and leaving the liquid to evaporate. They crystallise in large octahedrons having a dark-amethyst colour. The solutions are decomposed by boiling, and on cooling yield crystals of the alumina-alum. (Vohl.)

β. *Chromous Sulphates.*—When the metallic powder obtained by the action of potassium on chromic chloride is treated with dilute sulphuric acid, hydrogen is evolved, and a solution obtained, which exhibits the characters of a chromous salt (Péligot). The solution, mixed with ammonia and sal-ammoniac, absorbs oxygen, nitric oxide, acetylene, and allylene, but not carbonic oxide, ethylene, or tritylene. (Berthelot, Bull. Soc. Chim. [2], vii. 194.)

Potassio-chromous sulphate, $\mathrm{Cr''K^2(SO^4)^2 6H^2O}$, is obtained by dissolving potassic sulphate in a cold saturated solution of chromous chloride (i. 941), and adding alcohol till a precipitate begins to form. If the solution be then left for some weeks in a closed vessel, potassio-chromous sulphate crystallises from it in fine blue rhombic prisms, which turn green on exposure to the air. (Péligot.)

Sulphates of Cobalt.—The *neutral cobaltous salt*, $Co''SO^4.7H^2O$, occurs native as cobalt-vitriol or bieberite, sometimes in monoclinic crystals, but usually in stalactites and crusts, in the rubbish of old mines at Bieber, near Hanau, and at Leogang in Salzburg. It is prepared artificially by heating metallic cobalt with strong sulphuric acid, or by treating cobaltous oxide or carbonate with the dilute acid. The red solution, left to evaporate at ordinary temperatures, yields red crystals having the form of ferrous sulphate, and, like the latter, containing 7 at. water. At 20°—30°, on the other hand, it separates in crystals with 6 at. water, isomorphous with hexhydrated sulphate of magnesium (p. 601) (Mitscherlich). It dissolves in 24 pts. of cold water, and is insoluble in alcohol. It effloresces in the air, gives off its water of crystallisation when heated, and is thereby converted into the rose-red anhydrous salt, which bears a moderately strong red heat without decomposition, but is decomposed by continued strong ignition.—A flesh-coloured *basic sulphate*, insoluble in water, is formed by treating the solution of the neutral salt with a quantity of alkali not sufficient for complete precipitation.

Ammoniacal cobaltous sulphate, $Co''SO^4.6NH^3$, or *Sulphate of tetrammonio-cobaltoso-diammonium*, $N^2[Co''(NH^4)^4H^2]SO^4$, is a white powder, produced (according to H. Rose) by the action of dry ammonia-gas on anhydrous cobaltous sulphate; also (according to Frémy) by the action of aqueous ammonia on cobaltous sulphate.

Respecting the ammoniated cobalt-salts obtained by the action of ammonia on cobaltous salt in contact with the air, see COBALT-BASES, AMMONIACAL (i. 1051). On the pentammoniated cobaltic salts, see also C. D. Braun (Ann. Ch. Pharm. cxxxviii. 109; Bull. Soc. Chim. 1866, ii. 316).

Double Salts of Cobaltous Sulphate.—*Ammonio-cobaltous sulphate*, $Co''(NH^4)^2(SO^4)^2.6H^2O$, and *Potassio-cobaltous sulphate*, $Co''K^2(SO^4)^2.6H^2O$, are red double salts, isomorphous with the corresponding salts of iron, magnesium, and manganese.

Potassio-ferroso-cobaltous sulphate, $Co''Fe''K^4(SO^4)^4.12H^2O$, and the corresponding *ammonium-salt* are produced by spontaneous evaporation of a mixed solution of the component salts. They both crystallise in reddish, oblique, rhombic prisms, which oxidise and crumble to a yellowish-brown powder on exposure to the air. On dissolving this powder in water, the original double salt is reproduced. (Vohl, Ann. Ch. Pharm. xciv. 57; Jahresb. 1855, p. 312.)

Magnesio-cobaltous sulphate, $\overset{''}{Co}{}^3Mg''(SO^4)^4.28H^2O$, is found native (according to Winkelblech) at Bieber in Hesse, as a red stalactitic mass, also called *cobalt-vitriol*.

Potassio-magnesio-cobaltous sulphate, $Co''Mg'K^4(SO^4)^4.12H^2O$, and the corresponding *ammonium-salt* are formed on mixing the solutions of the component salts, and crystallise very easily in large rose-coloured, oblique, rhombic prisms, which give off all their water between 160° and 180°, assuming a fine light-blue colour. (Vohl.)

Potassio-manganoso-cobaltous sulphate, $Co''Mn''K^4(SO^4)^4.12H^2O$, and the corresponding *ammonium-salt*, prepared like the preceding, crystallise in fine red prisms and tables, the ammonium-salt being, however, more inclined to the tabular, the potassium-salt to the prismatic form. (Vohl.)

Potassio-niccolo-cobaltous sulphate, $Co''Ni''K^4(SO^4)^4.12H^2O$, and the corresponding *ammonium-salt*, prepared in like manner, crystallise in large tables and prisms having a dingy greenish-grey colour. (Vohl.)

Potassio-zinco-cobaltous sulphate, $Co''Zn''K^4(SO^4)^4.12H^2O$, and the corresponding *ammonium-salt* crystallise in rose-red prisms and tables. When heated to 180°, they give off all their water, assuming a blue colour, which partially disappears on cooling. The ammonium-salt leaves, after prolonged ignition, a fine green-coloured mass, from which water extracts only a portion of the cobaltous sulphate. (Vohl.)

Sulphates of Copper.—*a.* Cupric Salts. *Normal* (or *neutral*) *cupric sulphate*, $Cu''SO^4.5H^2O$, also called *Blue vitriol* and *Copper vitriol*.—This salt occurs very frequently as a secondary product, in mines where sulphuretted copper-ores undergo disintegration, and is found either crystallised in clefts and cavities, or dissolved in the waters of the mine, or in the water used for washing the ore.—It is produced artificially by boiling cupric oxide (scale-oxide of copper) with dilute sulphuric acid, and crystallises out on cooling; or by heating metallic copper with strong sulphuric acid, whereupon sulphurous oxide is evolved, and anhydrous cupric sulphate is precipitated as a white powder, mixed with a brown mass of cuprous and cupric sulphides (p. 340). On digesting this mass with hot water, the cupric sulphate dissolves out, and may be crystallised from the solution.

Cupric sulphate is extensively used in the arts, and is prepared on the large scale, either from artificially prepared sulphide of copper, or by roasting and lixiviation of sulphuretted copper-ores, or from the coarse copper (*Kupferstein*, ii. 27, 34) produced in the smelting of copper, and consisting mainly of the sulphides of copper and iron. The most usual mode of preparation is from artificial sulphide of copper. For this purpose, plates of copper (*e.g.*, old sheathings of ships' bottoms) are heated to strong redness on the hearth of a reverberatory furnace; a certain quantity of sulphur is then thrown in, and all the doors closed. The copper is thereby converted into sulphide, and as soon as the combination is complete, the draught of air is re-established, and the mass is heated to redness, whereby the sulphide of copper is oxidised to cupric sulphate and cupric oxide:

$$Cu^2S + O^5 = Cu''SO^4 + CuO.$$

The roasted mass is thrown, while still hot, into water containing sulphuric acid, and the resulting solution is evaporated to the crystallising-point. The crystals of cupric sulphate thus obtained are nearly pure.

The preparation of cupric sulphate by roasting copper-glance, purple copper, &c., or coarse copper, is precisely similar, and the solution obtained by lixiviating the roasted products also yields nearly pure cupric sulphate in the first and second crystallisations; but the mother-liquors contain a large proportion of ferrous sulphate, and frequently also salts of manganese, cobalt, &c., so that when evaporated to dryness they yield a very impure cupric sulphate: on this account it is better to precipitate the copper from these liquors by metallic iron, and then treat it with sulphuric acid.

Very pure cupric sulphate is obtained as a secondary product in the treatment of auriferous silver with sulphuric acid. From the solution of argentic sulphate thus produced, the silver is precipitated by metallic copper, and a solution of cupric sulphate is formed (ii. 925).

The blue vitriol of commerce is generally pure, with the exception of a small quantity of ferrous sulphate. From this it cannot be freed by mere recrystallisation, as the two salts are very apt to crystallise together isomorphously (p. 592); but if the solution be first heated with a little nitric acid, to convert the ferrous into ferric sulphate, it will then yield pure crystals of the cupric salt. The solution, after treatment with nitric acid, may also be digested with cupric oxide, which will precipitate the iron as ferric oxide. Another mode of removing the iron is to boil the solution with peroxide of lead, and precipitate the ferric oxide thereby produced with a small quantity of carbonate of barium. (Wurtz.)

Cupric sulphate crystallises with 5 at. water in large, azure-blue, triclinic prisms, having the form and modifications shown in *figs.* 313, 314, and 315 (CRYSTALLOGRAPHY, ii. 158). Angle $\infty\bar{P}\infty : \infty{,}P = 154° 3'$; $\infty\bar{P}\infty : \infty P'_{,} = 149° 7'$; $\infty\bar{P}\infty : \infty P' = 110° 10'$; $\infty\bar{P}\infty : \infty'P$ (behind) $= 126° 40'$; $\infty\breve{P}\infty : \infty\bar{P}\infty = 79° 19'$; $\infty P'_{,} : \infty{,}'P = 123° 10'$; $P' : \infty\breve{P}\infty = 103° 27'$; $P' : \infty P'_{,} = 127° 40'$; $P' : \infty\bar{P}\infty = 120° 50'$. The face $\infty\bar{P}\infty$ is striated parallel to the principal axis. The salt has a nauseous metallic taste and acid reaction. Specific gravity = 2·274 (Kopp); 2·302 (Buignet, Jahresb. 1861, p. 15). The crystals effloresce superficially on exposure to the air, give off 4 at. water at 100°, and the remaining 1 at. at 200°, leaving the anhydrous salt as a white saline mass, which is decomposed at a bright red heat, giving off sulphurous oxide and oxygen, and leaving cupric oxide. The anhydrous salt has a very powerful attraction for water, which it absorbs rapidly from the air, becoming hot and assuming a blue colour: on this account it is used for dehydrating alcohol.

Hydrated cupric sulphate dissolves in 3½ pts. of cold and in a much smaller quantity of boiling water. According to Poggiale, 100 pts. of water dissolve the following quantities at various temperatures:—

Temperature.	Quantities of salt dissolved.	
	Crystallised.	Anhydrous.
10°	36·9	20·9
20°	42·3	23·5
40°	56·9	30·3
80°	118·0	53·1
100°	203·3	75·3

Cupric sulphate is insoluble in absolute alcohol, and less soluble in hydrated alcohol as the proportion of alcohol is greater. According to Schiff (Ann. Ch. Pharm. cxviii. 362; Jahresb. 1861, p. 87), 100 pts. of spirit of various strengths, saturated with cupric sulphate ($CuSO^4.5H^2O$) at 15°, contain the following quantities of the pentahydrated salt:

Percentage of alcohol by weight	0	10	20	40
Quantity of salt in 100 pts.	27·2*	13·3	3·1	0·25

* This number, which gives the quantity of the hydrated salt dissolved in pure water at 15°, does not agree with Poggiale's determinations.

Hydrochloric acid dissolves cupric sulphate, with considerable reduction of temperature, forming a green liquid, which, when evaporated, yields crystals of cupric chloride. According to Kane, both the anhydrous salt and the pulverised hydrate rapidly absorb 2 at. hydrochloric acid gas.

When a strong solution of sugar is added to a strong solution of cupric sulphate, a white easily soluble precipitate is gradually formed, consisting of a compound of 1 at. cupric sulphate with 1 at. sugar ($C^{12}H^{22}O^{11}$) and 4 at. water. (**Barreswil**, J. pr. Chem. xxxv. 253.)

When a solution of cupric sulphate is mixed with ferrous sulphate, or with sulphate of zinc, magnesium, or nickel in excess, the cupric sulphate crystallises isomorphously with these salts in the most varying proportions, the crystals having the form of ferrous sulphate and containing 7 at. water. If, on the other hand, the cupric sulphate is in excess, the crystals have the form of blue vitriol, and contain 5 at. water (**Mitscherlich**). According to Rammelsberg, a solution containing 1 at. ferrous to 4 at. cupric sulphate yields crystals having the form of the latter.

Cupric sulphate is used for the preparation of many blue and green pigments (such as Bremer blue, Schweinfurt green, &c.), and very largely in the electrotype process. It is also used in medicine. Its purity may generally be recognised by the form and colour of the crystals. A tinge of green indicates the presence of a ferrous salt; blue vitriol thus contaminated does not dissolve completely in ammonia. The presence of zinc is easily recognised in the liquid which remains after precipitating the copper by sulphydric acid.

Basic Salts.—There are several basic cupric sulphates, forming greenish powders, and obtained for the most part by digesting a solution of the normal salt with cupric hydrate or carbonate, or by imperfect precipitation with potash. Some of them also occur native.

A *dicupric salt*, $2Cu''O.SO^3.H^2O$ or $Cu''SO^4.Cu''H^2O^2$, is produced, according to **Thompson**, by digesting the normal salt with cupric oxide in equivalent quantities; and the anhydrous salt, $2CuO.SO^3$ or $CuSO^4.CuO$, according to **Roucher** (J. Pharm. [3] xxxvii. 249; Jahresb. 1861, p. 193), as an orange-yellow pulverulent mass, by the normal salt to dullredness for several hours.

The *tricupric salt*, $3CuO.SO^3 = CuSO^4.2CuO$, is produced by the action of water on the anhydrous dicupric salt, which, when exposed to moist air, is converted into a green mixture of the normal salt and the salt $3CuO.SO^3.2\frac{1}{2}H^2O$; and when immersed in hot water, yields a solution of the normal salt, and a residue consisting of $3CuO.SO^3.3H^2O$.

The *tetracupric salt*, $4CuO.SO^3.3H^2O = CuSO^4.3CuH^2O^2$, occurs native as *brochantite* (i. 664), in emerald-green rhombic prisms, at Ekaterinenberg in Siberia, at Retzhanya in Hungary, and at Krisuvig in Iceland (*krisuvigite*). It is produced artificially:—1. By precipitating a solution of blue vitriol with a quantity of potash just sufficient to render the liquid alkaline; it then falls as a light-blue precipitate containing 3 at. water if separated from concentrated, and 5 at. water if from dilute solutions (**J. Denham Smith**). Kuhn found this precipitate to contain 4 at. water, and observes that the complete precipitation of the copper from 1 at. normal cupric sulphate ($CuSO^4$) requires exactly $\frac{3}{4}$ at. potash (KHO). According to **Field** (Phil. Mag. [4] xxiv. 123), the tetrahydrated salt, $4CuO.SO^3.4H^2O$ or $CuSO^4.3CuH^2O^2.H^2O$, is precipitated as a shining green powder, when a small quantity of potash is added to a large excess of blue vitriol, the liquid boiled, and the precipitate thoroughly washed. The same composition is exhibited by brochantite from Acandallo in Chile: specific gravity = 3·81.—2. The same hydrate is obtained, according to **Vogel** and **Reischauer** (Jahresb. 1859, p. 215), by precipitating blue vitriol with an insufficient quantity of ammonia. If the ammonia is added in excess, the tetrabasic salt is likewise formed, but mixed with cupric hydrate, from which however it quickly separates in microscopic crystals, while the cupric hydrate is converted into oxide.—3. The tetrabasic salt is also formed, mixed however with cupric hydrate, when metallic copper is left in a solution of ammonium-sulphate exposed to the air. (**Vogel** and **Reischauer**.)—4. The tetracupric salt with $3\frac{1}{2}$ at. water $= 2(CuSO^4.3CuO).7H^2O = 2(CuSO^4.3CuH^2O^2).H^2O$, is formed on mixing a dilute solution of blue vitriol with the acetate of an alkali-metal, magnesium, manganese, cobalt, nickel, zinc, cadmium, or copper; thus with sodic acetate:

$$4CuSO^4 + 6C^2H^3NaO^2 + 3H^2O = CuSO^4.3CuO + 3Na^2SO^4 + 6C^2H^4O^2.$$

The precipitate, which forms slowly in the cold (or with the acetates of zinc, nickel, and cobalt, not at all), but immediately on boiling, is flocculent at first, but soon becomes granular; it has a fine green colour, nearly equal to that of Schweinfurt green, and is so nearly insoluble in boiling water that it is perceptibly formed in liquids containing only $\frac{1}{50,000}$ pt. of sodic acetate; in dilute acids, on the contrary (even in acetic acid), it is easily soluble, and somewhat soluble in cupric sulphate. By repeated evaporation with sodic acetate it is gradually decomposed, with deposition of black cupric oxide, and formation of a blue sodio-cupric acetate. Tetracupric sulphate is also formed on mixing boiling solutions of normal cupric sulphate and formate, propionate, or valerate of sodium, but not with glycollate or lactate of sodium, or with lactate of zinc; further by mixing a solution of cupric acetate (or formate, propionate, valerate, or lactate) heated to 95°, with a boiling-hot solution of a sulphate, or by boiling it with dilute sulphuric acid. With sodic sulphate the reaction is:

$$Na^2SO^4 + 4C^4H^6Cu''O^4 + 3H^2O = CuSO^4.3CuO + 2C^2H^3NaO^2 + 6C^2H^4O^2;$$

with cupric sulphate it is represented by the equation:

$$CuSO^4 + 3C^4H^6CuO^4 + 3H^2O = CuSO^4.3CuO + 6C^2H^4O^2.$$

In either case the mixture must be repeatedly evaporated to dryness to expel the acetic acid. (Casselmann, Zeitschr. Anal. Chem. iv. 24; Jahresb. 1865, p. 272.)

A *pentacupric salt*, $5CuO.SO^3.H^2O = CuSO^4.4CuO.H^2O$ [?], is obtained, according to Denham Smith, as a light-blue precipitate, by treating blue vitriol with a slight excess of potash, and washing, pressing, and drying it as quickly as possible.

An *octocupric salt*, $8CuO.SO^3.12H^2O$, is obtained, according to Kane, by adding caustic potash to a solution of blue vitriol till the copper is completely precipitated. It is described as a grass-green powder, which gives off 6 at. water at 150°, and the remainder at 260°. Neither Smith nor Kühn was able to prepare the octobasic salt by this process: the latter always obtained the tetracupric salt.

A still more highly basic sulphate (containing only 5 to 7 per cent. SO^3) is produced, according to Vogel and Reischauer, by diluting a solution of ammoniacal cupric sulphate with a large quantity of water; but it is perhaps only a mixture. Indeed, it is doubtful whether any cupric sulphate more basic than the tetracupric salt has been obtained as a definite compound.

Ammoniacal Cupric Sulphates.—A solution of cupric sulphate mixed with excess of ammonia, forms a deep blue liquid, which, on addition of alcohol, yields crystals of the compound $Cu''SO^4.4NH^3.H^2O$; and this, when heated to 149°, yields the salt $CuSO^4.2NH^3$, or $N^2H^6Cu''SO^4$, as an apple-green powder. Anhydrous cupric sulphate rapidly absorbs dry ammonia-gas, and forms a blue powder consisting of $CuSO^4.10NH^3$. (See COPPER-BASES, AMMONIACAL, ii. 80.)

Double Salts.—*Ammonio-cupric sulphate*, $Cu''(NH^4)^2(SO^4)^2.6H^2O$, crystallises by evaporation of the mixed solutions of its component salts, in blue easily soluble crystals (Mitscherlich).—The corresponding *potassium-salt*, $Cu''K^2(SO^4)^2.6H^2O$, crystallises by spontaneous evaporation, in large, regular, light-blue, monoclinic crystals (Mitscherlich). By heating the crystals, the anhydrous salt is obtained as a green friable mass, which melts at a red heat, giving off part of its acid (Vogel). When cooled after fusion, it solidifies in a blue crystalline mass, which soon decrepitates and falls to powder (Graham, Phil. Mag. [3] iv. 418). It dissolves easily in water, and the solution, when heated to 60°, deposits a light-green crystalline powder, consisting of a basic double salt, $\overset{''}{Cu}{}^3K^2(SO^4)^4.Cu''O.4H^2O$ (Brunner, Pogg. Ann. l. 43), from which water extracts sulphate of potassium, leaving tetracupric sulphate.

By mixing the solutions of the ammonio- and potassio-cupric salts just described with the corresponding double sulphates of cobalt, iron, magnesium, manganese, nickel, and zinc, complex salts are obtained, having a composition which may be illustrated by that of the magnesium-salts, viz.:

$$Cu''Mg''(NH^4)^4(SO^4)^4.12H^2O \text{ and } Cu''Mg''K^4(SO^4)^4.12H^2O.$$

All these salts crystallise in monoclinic prisms and tables, isomorphous with the magnesium double salts (p. 602). Further, by mixing the solutions of three or four of these double salts, other salts of still more complex constitution may be formed, but still isomorphous with the preceding: *e.g.*, $Cu''Mn''Mg''K^6(SO^4)^6.18H^2O$, $Cu''Zn''Mg''(NH^4)^6(SO^4)^6.18H^2O$, and the corresponding potassium-salt; also $Cu''Co''Zn''Mg''K^8(SO^4)^8.24H^2O$. (Vohl, Ann. Ch. Pharm. xciv. 57; Jahresb. 1855, p. 311.)

Cobaltoso-cupric sulphate, $Cu''Co''^2(SO^4)^3.36H^2O$, obtained by evaporating a mixed solution of the component salts, crystallises like sulphate of cobalt. (Liebig.)

Ferroso-cupric Sulphate, also called *Salzburg Vitriol*, *Adlervitriol*, *Cuprum sulphuricum medium*.—It has already been mentioned that ferrous and cupric sulphates, though they crystallise separately in different forms, and with different quantities of crystallisation-water, are nevertheless capable of crystallising together in the form of ferrous sulphate—the cupric, like the ferrous salt, then taking up 7 at. water. Such composite salts (not true double salts) are obtained in bluish-green crystals in the preparation of cupric sulphate from ferruginous materials. The proportion between the copper and iron is very variable. A common proportion is that represented by the formula $CuFe^2(SO^4)^3.21H^2O$. The so-called Salzburg vitriol, prepared at Buxweiler in Alsace, is (according to Lefort) $CuFe^2(SO^4)^4.28H^2O$. In Admont vitriol the quantity of iron is to that of copper as 5 : 1; in double Admont vitriol, as 4 : 1; in Bayreuth vitriol, as 7 : 1.

Magnesio-cupric sulphate, $CuMg(SO^4)^2.14H^2O$, crystallises by spontaneous evaporation, in beautiful sky-blue tables and prisms. (Vohl.)

Sodio-cupric sulphate, $Cu''Na^2(SO^4)^2.2H^2O$(?)—A solution of blue vitriol and Glauber's salt deposits each of the salts separately; a solution of blue vitriol and acid sodic sulphate also yields blue vitriol and Glauber's salt separately at first, but afterwards small crystals of the double salt, united into a crust, and apparently containing 2 at. water. The double salt is easily dehydrated, melts at a commencing red heat without losing acid, and on cooling solidifies to a blue mass, which does not decrepitate like the potassic double salt. The sodio-cupric salt deliquesces slowly in the air, and is resolved by water into the two simple salts. (Graham, Phil. Mag. [3], li. 352.)

Zinco-cupric sulphate, $Cu''Zn''^3(SO^4)^4.28H^2O$, improperly called *Cyprian vitriol*, is prepared at Chessy near Lyons, from zinciferous copper-ores, and crystallises in blue rhombic prisms. (Lefort, Compt. rend. xxvi. 185.)

β. *Cuprous sulphate*, $\acute{Cu}^2SO^4 = Cu^2O.SO^3$, is (according to Berzelius) the black powder which remains undissolved when copper is heated with strong sulphuric acid; it dissolves in nitric acid, with evolution of nitric oxide. According to Mène, on the other hand, this insoluble residue is a mixture of cuprous and cupric sulphide with cupric oxide.

Sulphate of Didymium, $Di''SO^4$, is obtained by dissolving the oxide or carbonate in dilute sulphuric acid. (For the methods of separating it from sulphate of lanthanum, see LANTHANUM, iii. 468.) The solution is rose-coloured, and yields, by spontaneous evaporation, dark rose-coloured shining crystals having the form of oblique rhomboïdal prisms (Mosander), and cleaving readily and distinctly in a direction parallel to the base. They contain $3DiSO^4.8H^2O$ (Marignac), and are isomorphous with the similarly constituted hydrated sulphates of cadmium and yttrium (Rammelsberg, Pogg. Ann. cxv. 579). At 200°, they give off the whole of their water, leaving an anhydrous powder, which may be heated to redness without further alteration. Sulphate of didymium is more soluble in cold than in hot water. Its solution when heated, especially to the boiling-point, deposits a crystalline precipitate, containing $DiSO^4.2H^2O$. The anhydrous sulphate dissolves in water more readily than either of the hydrates. The following table exhibits the quantities of anhydrous sulphate in 100 pts. of water, in solutions formed by dissolving the anhydrous sulphate and the two hydrates in water at different temperatures (Marignac):

	Quantity of anhydrous salt to 100 pts. water in solution of		
Temperature.	anhydrous salt.	$DiSO^4.2H^2O$.	$3DiSO^4.8H^2O$.
12° C.	43·1		
14	39·3		
18	25·8	16·4	
19			11·7
25	20·6		
38	13·0		
40			8·8
50	11·0		6.5
100			1.7

The anhydrous sulphate exposed to the heat of an intense charcoal-fire, gives off two-thirds of its acid, and leaves a *tribasic sulphate*, $3DiO.SO^3$, or $DiSO^4.2DiO$. (Marignac). The same salt is obtained as a light-bluish rose-coloured hydrate, $3DiO.SO^3.8H^2O$, by precipitating a solution of the neutral sulphate with excess of ammonia. (Hermann, Jahresb. 1861, p. 197.)

Sulphate of didymium forms double salts with the sulphates of the alkali-metals.—The *ammonium-salt*, $\overset{\prime\prime\prime}{Di}{}^2(NH^4)^2(SO^4)^4.8H^2O$, dissolves in 18 times its weight of water.—The *potassium-salt*, $\overset{\prime\prime\prime}{Di}{}^2K^2(SO^4)^4.2H^2O$, dissolves in 63 pts. of cold water.—The *sodium-salt*, $Di'''^2Na^2(SO^4)^4$, is anhydrous, requires 200 pts. of water to dissolve it, and is still less soluble in solution of sodic sulphate. (Marignac.)

Sulphate of Erbium has, according to Marignac (Jahresb. 1864, p. 198), the composition $3Eb''SO^4.8H^2O$, and is isomorphous with sulphate of didymium.

Sulphates of Glucinum.—The *neutral salt*, $G''SO^4.4H^2O$, or $\overset{\prime\prime\prime}{Be}{}^2(SO^4)^3.12H^2O$ (ii. 849), is obtained by dissolving glucina or its carbonate in a slight excess of cold sulphuric acid, and crystallises, by spontaneous evaporation, in large quadratic octahedrons. Alcohol precipitates it from solution as a crystalline powder. It is very soluble in pure water, somewhat less soluble in acidulated water, insoluble in absolute alcohol. According to Debray, water at 15° takes up nearly its own weight of the crystals. The crystals effloresce in warm air, melt with strong intumescence when heated, and leave a residue of pure glucina. At 35° they give off 4 at. water and crumble to powder; between 100° and 110°, they retain only 1 at. water, which is regarded by Weeren as constitutional water. The solubility of the salt is not much diminished by dehydration; it does not give off any acid at 150°—200° (Weeren).—A *tribasic sulphate*, $3G''O.SO^3 = G''SO^4.2G''O$, or $Be^2O^3.SO^3$, is obtained, as a gummy opaque mass, by boiling the solution of the neutral salt with glucinic carbonate, as long as carbonic dioxide is given off, and leaving the solution to evaporate without previous dilution. If, on the other hand, the solution be diluted before evaporation, it deposits a *hexbasic salt*, $6GO.SO^3.3H^2O$, or $2Be^2O^3.SO^3.3H^2O$, in the form of a white powder; and the liquid filtered therefrom yields on evaporation a gummy mass, consisting of the *dibasic salt*, $2G''O.SO^3$, or $2Be^2O^3.3SO^3$.

Sulphates of Iridium.—*Iridic sulphate*, $Ir^{iv}O^2.SO^3 = Ir^{iv}(SO^4)^2.Ir^{iv}O^2$, is obtained by dissolving sulphide of iridium in nitric acid, and driving off the excess of acid by heat, as a thick yellow syrup, exhibiting no signs of crystallisation. It dissolves easily in water and in alcohol, forming orange-yellow solutions, which are not precipitated by alkalis. On drying the salt, half the acid is expelled, and a more highly basic salt, $2IrO^2.SO^3$, remains.—*Iridious sulphate*, $Ir''SO^4$, is produced by dissolving iridious hydrate in sulphuric acid, and separates, on evaporation at a gentle heat, as a brownish-green, shining, amorphous mass, which dissolves in water with dark yellow-green colour.

Sulphates of Iron.—*a. Ferric Salts.*—The *normal* (or *neutral*) *salt*, $\overset{'''}{Fe}{}^2(SO^4)^3 = Fe^2O^3.3SO^3$, occurs as a hydrate containing 9 at. water, at Coquimbo in Chile, in six-sided pyramids, and as a fine-grained mass, forming a layer several feet thick (see COQUIMBITE, ii. 83). It is produced artificially by heating brown hæmatite for some time with strong sulphuric acid, and then expelling the excess of acid by a gentle heat;—or, more generally, by adding 1 at. sulphuric acid to a solution of 2 at. ferrous sulphate, and then adding nitric acid by small portions as long as nitrous vapours are evolved:

$$2Fe''SO^4 + H^2SO^4 + O = \overset{'''}{Fe}{}^2(SO^4)^3 + H^2O.$$

According to Levol, this salt (and not ferrous sulphate) is formed when metallic iron is heated with strong sulphuric acid.—According to Bussy and Lecanu, the white deposit, formed during the concentration of the acid in sulphuric acid works, consists almost wholly of ferric sulphate, formed most probably by the accidental dropping of ferruginous substances into the acid.—The *anhydrous salt*, $\overset{'''}{Fe}{}^2(SO^4)^3$, is formed, according to P. Hart, on introducing ferrous sulphate into boiling concentrated sulphuric acid, and separates on cooling in very small crystalline scales. The same salt is described by Ulrich (Jahresb. 1859, p. 211) as occurring in the platinum-vessel used for concentrating sulphuric acid, at the vitriol-works of Oker in the Harz, in small, shining, peachblossom-coloured spangles, appearing under the microscope as rhombic octahedrons with truncated summits.

The red solution of ferric sulphate, obtained as above, leaves on evaporation a light-yellow deliquescent mass, consisting of the hydrated salt, still retaining a slight excess of acid. In this state it redissolves easily in water, but if it be gently heated till the water and excess of acid are expelled, the remaining anhydrous salt dissolves but very slowly in water, forming a reddish-yellow solution. The anhydrous salt is also nearly insoluble in hydrochloric acid, and quite insoluble in strong sulphuric acid, which indeed precipitates it from its solution.—The anhydrous salt is decomposed at a red heat, and is recommended by Berzelius for the preparation of sulphuric anhydride by dry distillation.

Basic Ferric Sulphates.—The *sesquibasic salt*, $Fe^2O^3.2SO^3 = 2Fe^2(SO^4)^3.Fe^2O^3$, is obtained (according to Maus) by digesting a concentrated solution of the normal salt with ferric hydrate, as a dark-red solution, which on boiling, or on dilution with water, is resolved into the soluble normal salt and an insoluble basic salt. The same salt is formed (according to Wittstein, Rep. Pharm. [3], i. 185), by the action of the air on ferrous sulphate, and constitutes the yellow crust, $Fe^2O^3.2SO^3.H^2O$, with which the crystals of this salt become covered after a while. It is resolved by water into the neutral and the *dibasic salt*, $2Fe^2O^3.3SO^3.8H^2O = Fe^2(SO^4)^3.Fe^2O^3.8H^2O$. According to H. Rose, this dibasic salt occurs, together with coquimbite, in yellowish-green, silky, fibrous masses.—Another *basic salt*, containing $2Fe^2O^3.5SO^3.18H^2O$, likewise occurs encrusting coquimbite. (H. Rose.)

The *tribasic salt*, $Fe^2O^3.SO^3 = Fe^2(SO^4)^3.2Fe^2O^3$, is produced, as a reddish-yellow powder, containing about 3 at. water, by dissolving the basic double salt of potassic sulphate and sesquibasic ferric sulphate (p. 597) in water, and heating the solution. (Soubeiran.)

The *hexbasic salt*, $2Fe^2O^3.SO^3 = Fe^2(SO^4)^3.5Fe^2O^3$, is, (according to **Berzelius**) the yellow precipitate which gradually forms in a solution of ferrous sulphate exposed to the air, according to the equation:

$$10(FeO.SO^3) + O^5 = 2Fe^2O^3.SO^3 + 3(Fe^2O^3.3SO^3);$$

but the composition of the precipitate most probably varies with the concentration of the solution.

The *nonobasic salt*, $2(3Fe^2O^3.SO^3).9H^2O = 2[Fe^2(SO^4)^3.8Fe^2O^3].27H^2O$, separates (according to Scheerer) as a brownish-yellow deposit, on evaporating an oxidised solution of ferrous sulphate, or when a neutral solution of ferric sulphate is diluted with a large quantity of water and boiled; also (according to Berzelius,) when a solution of ferrous sulphate is mixed with chlorate of potassium.

A *dodecabasic salt*, $4Fe^2O^3.SO^3 = Fe^2(SO^4)^3.11Fe^2O^3$, is formed (according to Anthon) in preparing ferric acetate by decomposing acetate of barium with soluble basic ferric sulphate, being precipitated as a bulky brown powder, together with the last portions of baric sulphate, from which it may be separated by levigation.—Another basic salt, containing $2(7Fe^2O^3.SO^3).21H^2O$, is found (according to **Scheerer**) as a dark-brown amorphous mass, in the alum-slate of Modum in Norway.

Double Salts.—***Aluminio-ferric sulphate*** occurs native in the quicksilver mines of Idria, in yellowish-white crystalline masses, containing 37·0 per cent. SO^3, 8·4 Fe^2O^3, 11·5 Al^2O^3, 43·0 water, and 1·0 insoluble residue; which, if the two bases are regarded as isomorphous, may be represented by the formula $(Al^2O^3;Fe^2O^3).3SO^3.15H^2O$. (Fehling.)

Ammonio-ferric sulphate, or *Ammonia-iron-alum*, $Fe'''(NH^4)(SO^4)^2.12H^2O$, or $\left.\begin{matrix}Fe^2O^3.3SO^3\\(NH^4)^2O.SO^3\end{matrix}\right\}.24H^2O$, is produced by mixing the solutions of ammonic and ferric sulphates, adding a little free sulphuric acid, and leaving the solution to evaporate. It is more stable than the corresponding potassium-salt, and crystallises more readily than the latter, in large, colourless, regular octahedrons. It is prepared on the large scale, for use in dyeing, being always employed when a perfectly neutral ferric salt is required.

A *basic ammonio-ferric sulphate*, $\left.\begin{matrix}Fe^2O^3.2SO^3\\2[(NH^4)^2O.SO^3]\end{matrix}\right\}.6H^2O$, is prepared (according to **Maus**) in the same manner as the corresponding potassium-salt, which it resembles very closely in form and other properties. Marignac, however, found for the salt thus prepared the composition $3Fe^2O^3.5(NH^4)^2O.12SO^3.18H^2O$. Berzelius mentions another basic ammonio-ferric sulphate (composition not specified), which he obtained as an ochry precipitate on dissolving iron in dilute sulphuric acid mixed with a little nitric acid, the ammonia being produced by the mutual action of the nitric acid and the water.

Cuprico-ferric sulphate, $\overset{\prime\prime\prime}{Fe}{}^2Cu''(SO^4)^4.24H^2O$, separates from a mixture of the component salts in equivalent proportions, containing a slight excess of sulphuric acid, on evaporating till a crystalline film begins to form, in bluish-green, microscopic, warty crystallisations (Bastick).—The corresponding *magnesium-salt* forms a warty mass; the corresponding *zinc-salt* crystallises in colourless prisms. (**Bastick.**)

Potassio-ferric sulphate, or *Potash-iron-alum*, $Fe''K(SO^4)^2.12H^2O$, or $\left.\begin{matrix}Fe^2O^3.3SO^3\\K^2O.SO^3\end{matrix}\right\}.24H^2O$, separates from a slightly acid mixture of the component salts, by spontaneous evaporation, in octahedral crystals, which in form and taste are undistinguishable from common alum. They are sometimes colourless, but often have an amethyst tint, arising (according to Heintz) from a trace of ferric acid. The salt does not, however, crystallise so readily as ammonia-iron-alum. To obtain large crystals, **Heintz** (Ann. Ch. Pharm. xliv. 271) triturates 10 pts. of crystallised ferrous sulphate with 4 pts. of saltpetre, then gradually adds 4 pts. of strong sulphuric acid, and heats gently as long as nitrous vapours continue to escape. The residue is thus dissolved in 3 or 4 pts. of water at 80°, and the filtered solution is left to crystallise at a temperature which is very slowly lowered to 0°.

Potash-iron-alum is not very stable, soon becoming covered with a yellow powder when exposed to the air at temperatures above 0°. Between 80° and 100° it is resolved into a basic potassio-ferric sulphate, neutral ferric sulphate, and free sulphuric acid:

$$\begin{aligned}2[(Fe^2O^3.3SO^3).(K^2O.SO^3).24H^2O] &= [(Fe^2O^3.2SO^3).2(K^2O.SO^3]\\ &\quad + (Fe^2O^3.3SO^3) + H^2O.SO^3 + 47H^2O.\end{aligned}$$

The aqueous solution likewise decomposes in the same manner when heated to 80°; but after keeping for some time, especially on addition of free sulphuric acid, it again yields, by spontaneous evaporation, crystals of the normal double salt. A solution of iron-alum, mixed with a large quantity of free sulphuric acid, does not decompose when evaporated over the water-bath, but deposits crystalline crusts containing $2Fe'''K(SO^4)^2.3H^2O$, and, on further concentration, a white powder, composed of $2Fe'''K(SO^4)^2.H^2O$. (Heintz.)

If potash be added to a concentrated solution of ferric sulphate or iron-alum till the precipitate no longer redissolves, the filtered solution yields, by spontaneous evaporation, olive-green or yellow six-sided tables of the basic salt $(Fe^2O^3.2SO^3).2(K^2O.SO^3).6H^2O$ (Maus).—Another *basic double salt*, $3(Fe^2O^3.2SO^3).2(K^2O.SO^3).22H^2O$, is produced (according to Soubeiran) on dropping carbonate of potassium into a solution of ferric oxide till the precipitate begins to become permanent, and mixing the clear solution with alcohol.—A third *basic double salt*, $4(Fe^2O^3.SO^3).(K^2O.SO^3).9H^2O$, occurs (according to Rammelsberg) as an ochre-yellow insoluble mass, in the lignite of Kaloforuk in Bohemia. (Handw. d. Chem. vii. 528.)

A *basic sodio-ferric sulphate*, $4(Fe^2O^3.SO^3).(Na^2O.SO^3).9H^2O$, analogous to the last-mentioned potassium-salt, occurs, as a light-yellow stalactitic mass, in the alum-slate of Modum in Norway.

β. Ferrous Sulphate, $Fe''SO^4.7H^2O$. *Green Vitriol. Copperas. Couperose. Eisenvitriol.*—This salt occurs native, sometimes in crystals, but more frequently massive and pulverulent, at Goslar in the Harz, at Hurlet near Paisley, in several of the Saxon and Hungarian mines, and at various localities in the United States, being formed by the oxidation of iron-pyrites. It may be obtained pure by dissolving 1 pt. iron or 1½ pt. ferrous sulphide in 1½ pt. sulphuric acid diluted with 4 pts. water. The solution, if quickly filtered, deposits the salt in beautiful, transparent, bluish-green, crystals, containing 7 at. water. The large quantities of ferrous sulphate consumed in the arts are however prepared, simultaneously with alum, by the decomposition of aluminous schists containing iron-pyrites (p. 580).

Ferrous sulphate forms well-defined monoclinic crystals, of prismatic or tabular character (*figs.* 285, 287, 289, 294, 298, 299, 308, 309, and 310: CRYSTALLOGRAPHY, ii. 152—156). Axes, $a:b:c = 0\cdot8476:1:1\cdot267$. Angle $b:c = 75°\ 40'$; $\infty P : \infty P$ (orthod.) $= 97°\ 39'$; $[P\infty] : [P\infty]$ (clinod.) $= 69°\ 15'$; $+P\infty : c = 43°\ 32'$; $-P\infty : c = 32°\ 36'$; $-\frac{1}{3}P\infty : c = 55°\ 20'$; $oP : \infty P = 80°\ 37'$. Cleavage perfect parallel to oP; less distinct parallel to ∞P. It is isomorphous with the heptahydrated sulphates of magnesium, zinc, cobalt, nickel, copper, &c. (p. 578).

The crystals of ferrous sulphate effloresce slightly in dry air, and if at all moist, absorb oxygen, and become covered with a reddish-yellow crust of basic ferric sulphate (p. 596); but if crushed, and deprived of hygrometric moisture by strong pressure between folds of cotton-cloth or filter-paper, they may be preserved in a bottle without change from oxidation (Graham). Ferrous sulphate, precipitated from its aqueous solution by alcohol, forms a bluish-white powder, which does not absorb oxygen unless exposed to very moist air. Another method of preserving it is to mix the pulverised crystals with an equal weight of gum-arabic, dissolve the whole in distilled water, evaporate over the water-bath to the consistence of an extract, pour the still hot mass upon porcelain plates, complete the desiccation in an oven at 30°, and preserve the dried salt in closely-stoppered bottles. (Parvesi, J. Pharm. [4] iii. 40.)

Crystallised ferrous sulphate gives off 6 at. water at 114°, but retains the last atom even at 280°; by very careful heating, however, it may be rendered perfectly anhydrous without appreciable loss of acid. The anhydrous salt is also obtained, in very small crystalline scales, by immersing the hydrated crystals in strong boiling sulphuric acid, and leaving the liquid to cool. At a red heat it decomposes, giving off sulphurous oxide, and leaving a basic ferric sulphate, which, when more strongly heated, ultimately leaves pure ferric oxide, known as *Colcothar vitrioli* or *Caput mortuum*.

The salt was observed by Mitscherlich to crystallise at 80° from a solution saturated at the boiling heat, with 4 at. water, in monoclinic prisms, isomorphous with the corresponding sulphate of manganese. When its solution, containing an excess of acid, is evaporated by heat, a saline crust is deposited, which (according to Kühn) contains $3H^2O$. Lastly, a dihydrate, $Fe''SO^4.2H^2O$, having the crystalline form and sparing solubility of gypsum, is obtained (according to Mitscherlich), by dissolving the ordinary crystals in strong sulphuric acid. A solution of the salt mixed with excess of sulphuric acid, and left to evaporate in a vacuum, first deposits the ordinary heptahydrated crystals, then greenish-blue crystals of a pentahydrate, $Fe''SO^4.5H^2O$, belonging to the triclinic system, and lastly crystals of the tetrahydrated salt. (Marignac.)

Ferrous sulphate dissolves easily in water, but is insoluble in alcohol. According to Brandes and Firnhaber, 1 pt. of the heptahydrated salt dissolves in the following quantities of water at the particular temperatures indicated above each quantity:—

10°	14°	25°	32·5°	46°	60°	84°	90°	100° C.
1·64	1·43	0·87	0·66	0·44	0·38	0·37	0·27	0·30

The solution has a slight bluish-green tint, or is colourless if very dilute. When exposed for some time to the air, it deposits a yellowish sediment of basic ferric sulphate, which is used in porcelain-painting. As soon, however, as a certain quantity of this salt is deposited, the oxidation ceases, and the solution remains almost unaltered. The partially oxidised solution may be reconverted into pure ferrous sulphate by boiling with metallic iron.

The solution of ferrous sulphate absorbs nitric oxide gas, assuming a dark-brown colour, which affords a very characteristic test for nitric acid (iv. 83). The brown solution has a powerful attraction for oxygen: if heated in close vessels, it gives off the gas for the most part unchanged; but when it is heated in contact with air, nitric acid is formed in the liquid, and converts the ferrous into a ferric salt.

Ferrous sulphate is largely used in dyeing and in tanning, and for the manufacture of ink and Prussian-blue. It is also very useful as a reducing agent in chlorimetry and other operations of analytical chemistry.

Ferrous sulphate forms, with the sulphates of potassium and ammonium, double salts containing 6 at. water isomorphous with the corresponding salts formed by the sulphates of zinc, copper, manganese, &c. The formula of the potassium-salt is $Fe''K^2(SO^4)^2.6H^2O$. The solution of this salt evaporated at 50°, yields a crystalline crust containing $Fe''K^2(SO^4)^2.2H^2O$. (Marignac.)

Ferrico-ferrous (or *Ferroso-ferric*) *sulphate*, $\overset{''}{Fe}{}^2\overset{'''}{Fe}{}^2(SO^4)^4$. or $(Fe''O.SO^3).(Fe^2O^3.3SO^3)$, is produced when a solution of ferrous sulphate is exposed to the air, till no more basic ferric sulphate is deposited. The solution, which is yellowish-red, does not crystallise, but yields black oxide of iron when precipitated by an alkali (Berzelius). Abich obtained a crystalline ferroso-ferric sulphate, containing $(3FeO.SO^3).2(Fe^2O^3.3SO^3)4H^2O$, or $\overset{''}{Fe}{}^3\overset{'''}{Fe}{}^4(SO^4)^9.4H^2O$, by heating a moderately strong solution of 16 pts. pure crystallised ferrous sulphate to the boiling-point with an equal weight of strong sulphuric acid, then adding 1 pt. of strong nitric acid, and a concentrated solution of 5 or 6 pts. alum. This solution, evaporated at a temperature below 70°, deposits a dark-brown crystalline powder, the solution of which, in water acidulated with sulphuric acid, yields the salt on evaporation, in nearly black shining crystals, which are combinations of the cube and regular octahedron. According to Barreswil, a salt having the same composition as Abich's, but of a dark-blue colour, is formed by mixing the solutions of 3 at. ferrous and 2 at. ferric sulphate, and slowly dropping sulphuric acid into the liquid as long as any blue precipitate is produced (Handw. d. Chem. vii. 532).—A *basic ferroso-ferric sulphate*, containing $(3FeO.2SO^3).3(Fe^2O^3.2SO^3).36H^2O$, is found in the copper-mines of Fahlun, in large red stalactites composed of small transparent crystals. (Berzelius.)

Magnesio-ferrous sulphate, $Fe''Mg''(SO^4)^2 14H^2O$, crystallises from a solution of the component salts, by spontaneous evaporation, in large sea-green crystals. (Vohl.)

Sodio-ferrous sulphate, $Fe''Na^2(SO^4)^2.4H^2O$, obtained by evaporation at 55°, is permanent in the air, and does not decompose at 100°; but on redissolving it, and leaving the solution to evaporate, the sodic and ferrous salts crystallise out separately.

Thallio-ferrous sulphate, $Fe''Tl^2(SO^4)^2.6H^2O$, has a pale-green colour, and is isomorphous with the corresponding potassium-salt. (Werther.)

Zinco-ammonio-ferrous sulphate, $Fe''Zn''(NH^4)^4(SO^4)^4.12H^2O$, and the corresponding *potassium-salt*, crystallise readily in large, greenish, oblique rhombic prisms and tables, which turn yellow in the air, from absorption of oxygen.

Sulphate of Lanthanum, $La''SO^4$, is prepared as described under LANTHANUM (iii. 468), and separates by spontaneous evaporation in small prismatic crystals containing $La''SO^4.3H^2O$. It gives off its water at a low red heat, and half its acid at a full red heat. It is much less soluble in hot than in cold water.—*Ammonio-lanthanic sulphate*, $\overset{''}{La}{}^3(NH^4)^2(SO^4)^4.8H^2O$, is obtained, by spontaneous evaporation of a dilute solution of lanthanum-sulphate mixed with a slight excess of ammonium-sulphate, in colourless, sparingly soluble, monoclinic crystals. (Marignac.)

Potassio-lanthanic sulphate, $La''K^2(SO^4)^2$, is formed as a white precipitate on mixing the solution of a lanthanum-salt with sulphate of potassium. (Hermann, Jahresb. 1861, p. 194.)

Sulphate of Lead, $Pb''SO^4 = Pb''O.SO^3$.—This compound occurs native as *Anglesite*, in large and beautiful crystals, at Pary's mine in Anglesea, Leadhills in Scotland, Wanlockhead in Derbyshire, and at Clausthal, Zellerfield, and Giepenbach in the Harz; also in Prussia, in the Black Forest, at Badenweiler in the Breisgau, in the

Island of Sardinia, and in the United States; also massive in Siberia, in Andalusia, and on Alston Moor in Cumberland. In Algeria it occurs (according to Marcel de Serres, Compt. rend. liv. 743), in kidney-shaped lumps enclosing a nucleus of galena, by the oxidation of which it has been formed.

The crystals of anglesite are trimetric and isomorphous with those of heavy spar (iii. 137), exhibiting generally the same faces, but with $\infty \breve{P} 2$ mostly predominant. Axes, $a : b : c :$ = 0·6089 : 1 : 0·7756. Angle $\infty P : \infty P$ (macr.) = 62° 40′; $\infty\breve{P}2 : \infty\breve{P}2$ (macr.) = 101° 13′; $\breve{P}\infty : \breve{P}\infty$ (basal) = 75° 35′; $\bar{P}\infty : \bar{P}\infty$ (basal) = 103° 43′. Cleavage imperfect parallel to $\infty\breve{P}\infty$ and $\bar{P}\infty$. Hardness = 2·75 to 3. Specific gravity = 6·295 to 6·298. Lustre highly adamantine in some specimens, in others inclining to vitreous and resinous. Colour white, tinged with yellow, grey, green, and sometimes blue. Streak uncoloured. Transparent to opaque. Fracture conchoïdal. Very brittle.

Sulphate of lead also occurs, combined with carbonate of lead, as *Lanarkite* (iii. 467), and as *Leadhillite* (iii. 560); also, with carbonate of lead and carbonate of copper, as *Caledonite* (i. 372).

Sulphate of lead may be artificially crystallised by fusing chloride of lead with sulphate of potassium, and boiling out the soluble salts with water; it then remains as a heavy white crystalline powder, which, even under a low magnifying power, is seen to consist of tabular crystals having the form of the native sulphate (Manross). It is usually obtained, as a heavy white crystalline powder, by precipitating a soluble lead-salt with sulphuric acid or a soluble sulphate; and on the large scale, as a secondary product, in the preparation of aluminic acetate by precipitating alum with acetate of lead. It is also produced by oxidising sulphide of lead with strong nitric acid.

Sulphate of lead is nearly insoluble in pure *water*; according to Rodwell (Chem. News, xi. 50), 1 pt. of it dissolves in 31,062 pts. water at 15°; also in dilute *sulphuric acid*, somewhat more easily in strong sulphuric acid; also in *nitric* and *hydrochloric acids*. According to Rodwell (Chem. Soc. Qu. J. xv. 59), 1 pt. of lead-sulphate dissolves in the following quantities of hydrochloric and nitric acids of various strengths:—

Hydrochloric acid.	Specific gravity.	HCl per cent.	Nitric acid.	Specific gravity.	N^2O^5 per cent.
681·89	1·0519	10·602	303·10	1·079	11·55
281·73	1·0800	16·310	173·75	1·123	17·50
105·65	1·1070	22·010	127·48	1·250	34·00
47·30	1·1359	27·525	10282·78	1·420	60·00
35·03	1·1570	31·602			

On dilution, all the hydrochloric acid solutions, except the first, deposit needles of plumbic chloride. The nitric acid solutions yield by evaporation octahedrons of plumbic nitrate. The sulphate, digested for three or four days with nitric acid containing 60 per cent. N^2O^5, is almost wholly converted into octahedrons of the nitrate.

It is dissolved in larger quantity by some *ammoniacal salts—e.g.*, by the sulphate, nitrate, acetate, and tartrate, and easily by caustic potash or soda. When boiled with a strong solution of *potassic* or *sodic carbonate* (best with the acid carbonates), it is decomposed like sulphate of barium, yielding a solution of alkaline sulphate and a deposit of carbonate of lead. According to Löwe (Jahresb. 1859, p. 685), sulphate of lead dissolves in aqueous *hyposulphite of sodium*, in consequence of the formation of sodio-plumbic hyposulphite. This reaction may be rendered available for separating sulphate of lead from sulphate of barium. According to Field (Chem. Soc. Qu. J. xvi. 28), nitrate of lead produces no precipitate in a mixture of sodic sulphate and hyposulphite. According to Städel (Jahresb. 1863, p. 245), 1 pt. lead-sulphate dissolves in 12·2 pts. of *calcic acetate* (in very dilute solution). It is slightly soluble also in *triplumbic acetate*, insoluble in *diplumbic acetate*.

Sulphate of lead melts at a red heat, without decomposition, unless in contact with silica or clay. On *charcoal* before the blowpipe, it is reduced to metallic lead, with evolution of sulphurous oxide. The products obtained by heating it with charcoal vary, however, according to the proportions used: thus—

$$2PbSO^4 + C = 2PbO + CO^2 + 2SO^2$$
$$PbSO^4 + C = Pb + CO^2 + SO^2$$
$$PbSO^4 + C^4 = PbS + 4CO.$$

When heated with *sulphide of lead*, as in the process of lead-smelting (iii. 482), it yields metallic lead, or a mixture of the metal and the protoxide, with evolution of sulphurous oxide:

$$PbSO^4 + PbS = 2SO^2 + Pb^2$$
$$2PbSO^4 + PbS = 3SO^2 + 2PbO + Pb.$$

Heated to redness in a stream of *hydrogen*, it is reduced to metallic lead, according to the equation,

$$2PbSO^4 + 7H^2 = Pb^2 + SO^2 + H^2S + 6H^2O.$$

The reduction of the sulphate by *carbonic oxide* is much more difficult, and requires a much higher temperature; in consequence of which a portion of the sulphide of lead formed at first, as represented by the equation

$$2PbSO^4 + 6CO = Pb + PbS + SO^2 + 6CO^2,$$

acts upon the undecomposed sulphate as above, and thus complicates the reaction. (Rodwell, Chem. Soc. Qu. J. xvi. 42.)

Iron and *zinc*, in contact with water, reduce sulphate of lead to a spongy mass of metallic lead. When triturated with a solution of *potassic chromate*, it yields chrome-yellow. Like all other lead-salts, it is blackened by *sulphydric acid*.

Sulphate of lead, as commonly prepared, is not adapted for painting, on account of its crystalline character and transparency; but by mixing litharge to a paste, with water containing a small quantity of acetate of lead, and gradually adding sulphuric acid, the sulphate may be obtained in the amorphous state, and mixed with a large excess of oxide of lead. In this state it has considerable body, and may be used instead of ordinary white lead. (Richardson.)

A *basic sulphate of lead*, $2PbO.SO^3 = PbSO^4.PbO$, is obtained (according to Kühn) by digesting the recently precipitated normal sulphate with aqueous ammonia.

Ammonio-plumbic sulphate, $Pb''(NH^4)^2(SO^4)^2$, is produced by precipitating a moderately concentrated solution of plumbic acetate with excess of sulphuric acid, neutralising the liquid with ammonia, and heating it to the boiling-point. If a sufficient quantity of ammoniacal salt is present, the precipitate dissolves completely, and the solution on cooling deposits the double salt, in slender, shining, transparent crystals. If no crystals separate, the liquid must be again heated till a precipitate begins to form; the liquid will then deposit crystals on cooling. Water decomposes the double salts, extracting 39·4 per cent. ammonium-sulphate, and leaving 60·6 per cent. plumbic sulphate. The crystals when heated yield a sublimate of ammonium-sulphite. (Wöhler.)

A compound of *sulphate* and *chloride of lead* was obtained by Becquerel (Ann. Ch. Pharm. lxxxiv. 199), in needle-shaped crystals, together with other products, by the action of galena on a solution of cupric sulphate and sodic chloride, continued for seven years.

Sulphate of Lithium, $Li^2SO^4.H^2O$.—This salt may be prepared by decomposing the carbonate or chloride with sulphuric acid,—or, better (according to Fuchs), from triphyllin. 8 pts. of this mineral, finely pounded, are stirred up with 6 pts. of water; 3½ pts. of nitric acid (of specific gravity 1·20) and 1½ pts. of strong sulphuric acid are then added; the whole is evaporated to dryness; the dry mass exhausted with water; the solution precipitated with ammonia and sulphide of ammonium, and then with oxalate of ammonium; the filtrate evaporated to dryness; and the residue ignited. The aqueous solution of the residue yields the salt in crystals. Sulphate of lithium crystallises in flat prisms or tables containing 1 at. water. It melts easily, and dissolves in water and in alcohol. Respecting the expansion of the aqueous solution by heat, see Kremers (Jahresb. xiv. 61).

Potassio-lithic sulphate, $Li^2K^4(SO^4)^3$, forms crystals belonging to the hexagonal system (Schabus).—*Sodio-lithic sulphate* crystallises, (according to Mitscherlich) in acute rhombohedrons.

Sulphate of Magnesium, $Mg''SO^4.7H^2O$. *Bitter Salt. Epsom, Seidlitz*, or *Saidschütz Salt. Epsomite. Sal amarum, s. anglicum, s. catharticum.*—This salt is very widely diffused in nature, occurring sometimes in the solid state, but much more abundantly in solution in sea-water and saline springs. It occurs as *Epsomite*, or *Hair-salt*, in silky fibres and fibrous crusts, at Idria in Carniola, at the gypsum quarries of Montmartre near Paris, in Fitou, Dept. of the Aude (France), in Arragon and Catalonia, in the Cordillera of St. Juan in Chile, and in a grotto in South Africa, where it forms a layer 1½ inch thick. The floors of the limestone caves in Kentucky, Tennessee, and Indiana are in many instances covered with minute crystals of epsomite mingled with the earth. In the Mammoth Cave, Kentucky, it adheres to the roof in loose masses, like snowballs. It is said to occur also in California and at Marmora in Canada West. (Dana.)

A monohydrated sulphate of magnesium, called *Kieserite*, occurs, mixed with the anhydrous sulphite, in the salt-beds of Stassfurth, forming granular lumps.

Sulphate of magnesium constitutes the purgative principle of bitter-waters, as those of Epsom in Surrey, and of Seidlitz, Saidschütz, and Püllna in Bohemia. It is often produced by the mutual action of magnesic carbonate and gypsum, as when a solution of gypsum remains for a long time in contact with a magnesian limestone. At Saidschütz, Seidlitz, and Püllna it is obtained by digging pits in the marl; in these the bitter-water gradually collects, in consequence of the reaction just mentioned, and on subsequently leaving the water to evaporate in shallow pans, the sulphate of magnesium crystallises out.

Sulphate of magnesium is prepared in considerable quantities from sea-water and saline springs, either by precipitating the magnesia with lime, and then dissolving it in sulphuric acid; or by first crystallising out the greater part of the common salt, and then treating the mother-liquor, which contains chloride of magnesium, either with sulphuric acid or with ferrous sulphate, whereby sulphate of magnesium and ferrous chloride are obtained, the latter remaining in solution when the liquor is further evaporated, while the sulphate of magnesium crystallises out. Respecting Balard's improved process for obtaining sulphate of magnesium and chloride of potassium from the mother-liquors of sea-water, see POTASSIUM-SALTS (iv. 717); also Richardson and Watts's *Chemical Technology* (vol. i. pt. iii. pp. 157, 538).

Sulphate of magnesium is also produced in considerable quantities by treating native carbonate of magnesium or dolomite with sulphuric acid; the gypsum formed in the latter case, being much less soluble than the magnesian sulphate, is easily separated from it. Sometimes the dolomite is burnt, the lime dissolved out by pyroligneous acid, and the residual magnesia treated with sulphuric acid (Henry). Serpentine, which is composed of hydrate and silicate of magnesium, may also be used as a source of magnesic sulphate. In the neighbourhood of Genoa, the serpentine of the locality, which is intersected with veins of iron and copper pyrites, is roasted, then exposed to the air for a long time, and lixiviated. From the liquor thus obtained, the copper is precipitated by iron; the ferrous oxide is peroxidised by chlorine; the resulting ferric oxide is precipitated by burnt lime or dolomite; and the clarified solution, which contains sulphate of magnesium, is evaporated to the crystallising-point.

Sulphate of magnesium crystallises on cooling, from a hot moderately concentrated solution, in large, four-sided, right rhombic prisms, containing 7 at. water, and isomorphous with the heptahydrated sulphates of zinc and nickel, also with chromate of magnesium. The most common form is the combination $\infty P . \frac{P}{2}$—that is to say, a vertical prism terminated by dome-shaped summits placed in opposite directions above and below (*fig.* 281, ii. 150). Axes $a : b : c = 0·989 : 1 : 0·5703$. Angle $\infty P : \infty P = 89° 22'$. Cleavable parallel to $\infty\breve{P}\infty$. The commercial salt is usually crystallised in small needles, obtained by rapid crystallisation from a very strong solution. The crystals are not efflorescent, but the commercial salt sometimes becomes moist in contact with the air, from adhering chloride of magnesium.

A boiling concentrated solution, if transferred while still hot to a well-closed vessel, often remains liquid and in a state of supersaturation, for a long time after cooling; but if exposed to a low temperature, it solidifies entirely to a crystalline mass. Sometimes, however, such a solution, after keeping for weeks or months, deposits milk-white prisms containing 6 at. water, and sometimes crystals containing 7 at. water, but differing in form from the ordinary crystals (Löwel, Ann. Ch. Phys. [3], xliii. 405; Jahresb. 1855, p. 345). These heptahydrated crystals were formerly supposed, according to Marignac's determinations (Jahresb. 1857, p. 150), to be rhombohedral (oR . + R . + R . − 2R); but Kopp has shown (Ann. Ch. Pharm. cxxv. 369; Jahresb. 1863, p. 192) that they are monoclinic prisms $\infty P . oP . +P\infty$, rendered tabular by predominance of $+P\infty$. The heptahydrated salt appears, therefore, to be dimorphous, a property which is further illustrated by the existence of the monoclinic double salt, $Fe''Mg''(SO^4)^2.14H^2O$, or $Fe''SO^4.7H^2O + Mg''SO^4.7H^2O$, and others of similar composition (pp. 594, 598).

A solution of magnesic sulphate, concentrated till a crystalline film begins to form upon it, and then left to crystallise at 30°, deposits the hexhydrated salt, $Mg''SO^4.6H^2O$, in small monoclinic crystals, isomorphous with the corresponding hydrated sulphates of zinc and nickel. Axes, $a : b : c = 0·7123 : 1 : 1·1841$. Angle $b : c = 81° 26'$; $\infty P : \infty P$ (orthod.) $= 108° 28'$; $oP : \infty P = 85° 0'$. Ordinary combination, $oP . \infty P$, with $-P$, $+\frac{1}{2}P$ and $+2P$, &c. subordinate.—A solution, crystallised at a temperature several degrees below 0°, deposits (according to Fritzsche) large crystals containing 12 at. water, of which, however, 5 at. are given off as soon as the temperature rises to 0°.

The ordinary heptahydrated crystals melt in their water of crystallisation when heated, and give off 6 at. water at 150°, but retain the seventh atom even at 200°. This last atom of water, designated by Graham as "constitutional water," may be replaced by various salts, giving rise to double salts. The anhydrous salt is a white mass, which melts at a red heat, but is only partially decomposed at very high temperatures.

Sulphate of magnesium is very soluble in water. 100 pts. of water dissolve 25·76 pts. of the anhydrous salt at 0°, and 0·47816 pts. for every degree beyond (Gay-Lussac). One pt. of the heptahydrated salt dissolves in 0·790 pts. water at 18·75.

forming a liquid of specific gravity 1·2932 (Authon). The following table exhibits the quantities of magnesic sulphate contained in solutions of different specific gravities, as determined by Schiff (Ann. Ch. Pharm. cviii. 336):

Specific gravity at 23°.	Per cent. of $MgSO^4.7aq$.	Per cent. of $MgSO^4$.	Specific gravity at 23°.	Per cent. of $MgSO^4.7aq$	Per cent. of $MgSO^4$.
1·0048	1	0·488	1·1426	28	13·660
1·0096	2	0·975	1·1481	29	14·148
1·0144	3	1·463	1·1536	30	14·634
1·0193	4	1·951	1·1592	31	15·122
1·0242	5	2·439	1·1648	32	15·610
1·0290	6	2·928	1·1704	33	16·098
1·0339	7	3·416	1·1760	34	16·586
1·0387	8	3·904	1·1817	35	17·074
1·0437	9	4·392	1·1875	36	17·562
1·0487	10	4·878	1·1933	37	18·050
1·0537	11	5·366	1·1991	38	18·538
1·0587	12	5·854	1·2049	39	19·026
1·0637	13	6·342	1·2108	40	19·512
1·0688	14	6·830	1·2168	41	20·000
1·0739	15	7·318	1·2228	42	20·488
1·0790	16	7·806	1·2288	43	20·976
1·0842	17	8·294	1·2349	44	21·464
1·0894	18	8·782	1·2410	45	21·952
1·0945	19	9·270	1·2472	46	22·440
1·0997	20	9·756	1·2534	47	22·928
1·1050	21	10·244	1·2596	48	23·416
1·1103	22	10·732	1·2659	49	23·904
1·1156	23	11·220	1·2722	50	24·390
1·1209	24	11·708	1·2786	51	24·878
1·1262	25	12·196	1·2850	52	25·366
1·1316	26	12·684	1·2915	53	25·854
1·1371	27	13·172	1·2980	54	26·341

Sulphate of magnesium is insoluble in absolute alcohol, moderately soluble in hydrated alcohol. According to Schiff (Ann. Ch. Pharm. cxviii. 365):

A solution (saturated at 15°) in alcohol of:		Contains per cent. of
Specific Gravity	Per cent. by weight.	$MgSO^4aq$.
1·000	0	50·8
0·986	10	39·3
0·972	20	21·3
0·939	40	1·62

(See, further, Storer's *Dictionary of Solubilities*, vol. iii. pp. 609—612.)

Sulphate of magnesium may be used, in localities where it occurs native, as a substitute for sulphuric acid in the decomposition of common salt. When 2 pts. of the ordinary crystallised sulphate are heated with 1 pt. of common salt, hydrochloric acid is evolved, and a residue is obtained, consisting chiefly of sulphate of magnesium and sulphate of sodium (Ramon de Luna). Respecting Clemm's process for preparing sulphuric acid from kieserite, ($MgSO^4.H^2O$), or from common sulphate of magnesium, and for decomposing common salt and chloride of potassium with kieserite, see Richardson and Watts's *Chemical Technology*, vol. i. pt. v. p. 266. A mixture of common salt, peroxide of magnesia, and sulphate of magnesium may be used for the preparation of chlorine. (De Luna.)

An *acid sulphate of magnesium*, $Mg''H^2(SO^4)^2$, is produced by dissolving the anhydrous neutral sulphate in hot concentrated sulphuric acid. The perfectly saturated syrupy solution deposits the acid salt on standing, in shining six-sided tables, which, however, rapidly absorb water and are thereby decomposed. (Schiff, Ann. Ch. Pharm. cvi. 115.)

Double Salts.—Sulphate of magnesium unites with the sulphates of ammonium, potassium, and thallium, forming double salts, which contain 6 at. water, and, as already observed, may be regarded as formed from the heptahydrated sulphate by the substitution of 1 at. K^2SO^4, &c. for 1 at. H^2O. They crystallise in monoclinic prisms, isomorphous with the corresponding ferrous salts, &c. (pp. 593, 598). The several salts of this isomorphous group do not exhibit exactly the same angles, but the differences are but small. As an average, the ratio of the axes, $a : b : c = 1·4 : 1 : 0·67$. Angle

$b : c = 74° 30'$. The crystals generally exhibit the faces $\infty P . oP . + P . + 2P\infty . P\infty$; often also $[\infty P2]$ and $\infty P\infty$, but mostly subordinate; also $- P$, &c. They are usually prismatic in the direction of the principal axis, or tabular from predominance of oP; rarely pyramidal or rhombohedral.

Potassio-magnesic sulphate $Mg''K^2(SO^4)^2.6H^2O$, is obtained, as a secondary product, in the preparation of common salt from sea-water and brine-springs (iv. 717), separating from the mother-liquors when concentrated to 34° Baumé in large hard crystals, which may be purified by recrystallisation. It also separates from a solution of its component salts, by cooling or evaporation. It is nearly as soluble as sulphate of magnesium.

Sulphate of magnesium also unites directly with other heptahydrated sulphates of diatomic metals, forming salts containing $14H^2O$, which, as they are formed without replacement of any portion of the water by another salt, may for distinction be called coupled or composite salts (*gepaarte Salze*: Vohl)—*e.g.*, *Magnesio-ferrous sulphate*, $Mg''Fe''(SO^4)^2.14H^2O$. (p. 598); and these composite salts are further capable of uniting with alkaline sulphates, forming double salts in which 2 at. water out of the 14 are replaced by 2 at. of an alkaline sulphate—*e.g.*, $Mg''Cu''K^4(SO^4)^4.12H^2O$.

Potassio-ferroso-magnesic sulphate, $Mg''Fe''K^4(SO^4)^4.12H^2O$, and the corresponding *ammonium-salt* crystallise in large, greenish, oblique, rhombic prisms and tables, which turn yellow on exposure to the air. (Vohl.)

Potassio-calcio-magnesic sulphate, $Mg''\overset{\prime\prime}{Ca}{}^2K^2(SO^4)^4.2H^2O$, occurs in the salt-beds of Stassfurth, and other localities, forming the mineral called polyhalite (iv. 687, 718).

Sodio-magnesic sulphate, $Mg''Na^2(SO^4)^2.6H^2O$, separates in rhombohedral crystals, from the liquors obtained in the preparation of Epsom-salt. It dissolves in 3 pts. of cold water, is permanent in the air, decrepitates when heated, and gives off its water without melting. A sodio-magnesic sulphate with 8 at. water, is found (according to Munoz y Luna) in the form of efflorescences, on the bottoms of numerous lakes which dry up in summer, in the province of Toledo, between Madrid and the Mediterranean. It forms large, transparent, regular, prismatic crystals.

Sulphates of Manganese.—α. *Manganic Sulphate*, $\overset{\prime\prime\prime}{Mn}{}^2(SO^4)^3 = \overset{\prime\prime\prime}{Mn}{}^2O^3.3SO^3$.—This salt does not crystallise, and was formerly known only in solution; but, according to Carius, it may be obtained in the solid state by triturating very finely-divided manganic peroxide (prepared by passing chlorine into a solution of sodic carbonate in which manganous carbonate is suspended) to a thin paste with strong sulphuric acid, heating the mass very gradually to about 138° (at which temperature it exhibits a deep green colour), then placing it on a warm plate of pumice to absorb the excess of sulphuric acid, triturating it in a warm porcelain mortar with strong nitric acid, afterwards absorbing this acid by pumice, and repeating this treatment six or eight times—finally heating the mass in a porcelain dish to 130°, till all the nitric acid is driven off, and quickly transferring the product to dry glass vessels.

Manganic sulphate thus prepared is a deep green perfectly amorphous powder. It may be heated with sulphuric acid to the boiling-point of the latter without decomposition; but on continued boiling, it gives off oxygen, and gradually dissolves as manganous sulphate. It is insoluble in nitric acid; but strong hydrochloric acid dissolves it, forming a brown solution, which gives off chlorine when heated. It absorbs moisture rapidly from the air, and small quantities of it deliquesce instantly to a clear violet viscid solution, which, however, soon becomes turbid from separation of manganic hydrate. It is quickly decomposed by water, and by dilute acids. With organic bodies it reacts like a mixture of manganic peroxide and sulphuric acid, but much more quickly. When heated with a large quantity of sulphuric acid, and a small quantity of water, it is converted into a red-brown basic manganic sulphate. (Carius, Ann. Ch. Pharm. xcviii. 54.)

Manganic sulphate unites directly with the *sulphates of potassium and ammonium*, forming alums.—The *potassium-salt*, $Mn'''K(SO^4)^2.12H^2O$, obtained by mixing the concentrated red solution of manganic sulphate with a saturated solution of potassic sulphate, and evaporating to a syrup at a gentle heat, crystallises on cooling in dark-violet octahedrons. It is resolved by water into its component salts.—The *ammonium-salt* resembles it exactly in external appearance.

β. *Manganous sulphate*, $Mn''SO^4$, is occasionally found native together with ferrous sulphate and zinc-sulphate. It is prepared by dissolving manganous carbonate in dilute sulphuric acid, or by heating any of the higher oxides of manganese (generally the native peroxide) with strong sulphuric acid, till the evolution of oxygen ceases, and the mass has become dry. This residue, after being then strongly ignited to decompose the iron-salt present, yields, by lixiviation with water, a solution of manganous sulphate free from iron. A process, much used on the large scale, consists in igniting manganic peroxide in a gas retort with about one-tenth of its weight of pounded coal, and dissolving the manganous oxide thus obtained in sulphuric acid, adding a little hydrochloric acid at the last, to reduce any remaining portion of the higher oxides of manganese.

Manganous sulphate crystallises, though with some difficulty, from a solution evaporated and left to itself, the proportion of water contained in the crystals varying with the temperature at which they are deposited. Below + 6°, crystals are formed containing 7 at. water, and isomorphous with ordinary ferrous sulphate; but those deposited between 7° and 20° contain 5 at. water, and are isomorphous with cupric sulphate. The heptahydrated salt melts at 18°, and the liquid, if further evaporated, deposits a salt containing $2H^2O$. The heptahydrate effloresces in dry air at 10° to 12°, and is converted into the hexhydrate $MnSO^4.6H^2O$, which at 18° gives off 2 at. more of water, leaving the tetrahydrate. The heptahydrated salt covered with absolute alcohol, and exposed for some days to a temperature of 10°, is converted into a powder containing 5 at. water, but at 20° into a powder containing only 4 at. water (**Brandes**). Between 20° and 30° a solution of manganous sulphate yields the tetrahydrate $MnSO^4.4H^2O$, in monoclinic prisms, isomorphous with tetrahydrated ferrous sulphate, and exhibiting the combination, $\infty P . \infty P2 . [\infty P\infty]$, with oP and $[P\infty]$ at the ends. Axes, $a : b : c : = 1{\cdot}157 : 1 : 0{\cdot}6783$. Angle $b : c + 89° 7'$; $\infty P : \infty P$ (orthod.) $= 81° 40'$; $\infty P2 : \infty P2$ (orthod.) $= 46° 44'$; $[P\infty] : [P\infty]$ (basal) $= 119° 10'$; $oP : \infty P = 89° 20'$.—These crystals give off 3 at. water at 115°, but retain the last at 200°. According to Kühn, a strongly acid and concentrated solution of manganous sulphate yields, by evaporation, a granular salt containing 1 at. water. Of all these hydrates, that containing 4 at. water is of most frequent occurrence. The crystals of manganous sulphate are colourless, or have a faint amethyst-red tint, due probably to a trace of manganic salt. The anhydrous salt dissolves, according to Brandes, in 2 pts. water at 15°, and in 1 pt. at 50°; at higher temperatures it is more soluble.

It is insoluble in absolute alcohol, moderately soluble in weak spirit.

Ammonio-manganous sulphate, $Mn''(NH^4)^2(SO^4)^2.6H^2O$, prepared by mixing the solutions of the component salts, and evaporating, forms deliquescent monoclinic crystals, isomorphous with the corresponding magnesium-salt. (**Mitscherlich.**)

Potassio-manganous sulphate, $Mn''K^2(SO^4)^2.6H^2O$, is obtained (according to **Mitscherlich**,) in like manner, and crystallises in similar form. **Marignac**, on the other hand (Ann. Min. [5] ix. 1; Jahresb. 1856, p. 381), by mixing equivalent quantities of manganous sulphate and potassic sulphate, and evaporating the solution in a vacuum at 10° to 12°, or by cooling a solution saturated at ordinary temperatures to 0°, never obtained the hexhydrated salt, but always the tetrahydrate, $Mn''K^2(SO^4)^2.4H^2O$, in monoclinic crystals,—a result confirmed by v. **Hauer** (J. pr Chem. lxxiv. 431; Jahresb. 1858, p. 170). The tetrahydrated salt was also previously obtained by **Pierre** (Ann. Ch. Phys. [3], xvi. 239). The same solution, left for some time at 40° to 50°, yields pale-red triclinic crystals of the dihydrate $Mn\ K^2(SO^4)^2.2H^2O$. (**Marignac.**)

Sodio-manganous sulphate, $Mn'Na^2SO^4$, crystallises by spontaneous evaporation in monoclinic crystals, containing $4H^2O$; and at 40° to 50°, in triclinic crystals with 2 at. water. (**Marignac**, *loc. cit.*) The dihydrated salt was previously obtained in a similar manner by **Arrott** (Ann. Ch. Pharm. lii. 243). It is not efflorescent, and bears a temperature of 100° without decomposition.

Ammonio-ferroso-manganous sulphate, $Mn''Fe''(NH^4)^4(SO^4)^4.12H^2O$, and the corresponding *potassium-salt*, also the corresponding *zinco-manganous salts*, crystallise in monoclinic prisms and tables; the zinc-salts are colourless; the ferrous salts have a tinge of green, and oxidise on exposure to the air. (**Vohl.**)

Sulphates of Mercury.—*a. Mercuric Salts.*—The *neutral salt*, $Hg''SO^4$ or $Hg''O.SO^3$, is prepared by boiling 4 pts. of mercury with 5 pts. of strong sulphuric acid, till sulphurous oxide is no longer evolved, and the whole is converted into a dry saline mass; or by dissolving 2 pts. of finely pulverised mercuric oxide in 1 pt. sulphuric acid diluted with 4 to 6 pts. water, and evaporating with constant stirring. Eissfeldt obtained it, in crystals containing 1 at. water, by heating mercury with sulphuric acid, as above, till the mass no longer became moist on exposure to the air; then spreading it out in a thin layer, and just covering it with water; the hydrated salt then separated, in the course of an hour, in colourless quadratic prisms, several lines long. The 1 at. water is given off at 100°.

Mercuric sulphate has a sharp, saline, disgusting metallic taste. It bears an incipient red heat without alteration, but melts at a higher temperature to a brown liquid, and volatilises completely to a white crystalline sublimate—a small portion, however, suffering decomposition. When heated in hydrochloric acid gas, it is converted into mercuric chloride, and is decomposed in like manner by dry hydriodic and hydrocyanic acids. In the wet way it is decomposed by all hydracids. By water it is resolved into a soluble acid salt, and an insoluble basic salt.—The *acid salt*, $Hg''O.3SO^3 = Hg''SO^4.2SO^3$, is obtained, by evaporating the filtered solution, in white needle-shaped crystals which absorb moisture from the air.—The *basic salt*, $3Hg''O.SO^3 = Hg''SO^4.2Hg''O$, formerly called *mineral turpethum*, or *turbith mineral*, is prepared by boiling the neutral salt with water, or by precipitating a hot dilute solution of mercuric nitrate with sulphate of sodium. It forms a lemon-yellow powder, which turns grey on exposure to the air, is very slightly soluble in cold, somewhat more in hot water. When heated, it is resolved into mercuric oxide and the neutral salt.

Both the neutral and the basic sulphate are converted by aqueous ammonia into sulphate of tetramercurammonium, or ammoniacal turpethum, $(N^2Hg^4) SO^4.2H^2O$ (iii. 928).

Ammonio-mercuric sulphate, $3Hg''(NH^4)^2(SO^4)^2.2H^2O$ [?], obtained by mixing the solution of the component salts, is slightly soluble in water, more soluble in excess of ammonia, and crystallises in large, oblique, rhombic prisms, which blacken on exposure to light. It appears to be analogous in composition to the potassium-salt, but its analysis could not be made with accuracy, as the crystals were covered with a fine powder of ammoniacal turpethum. (Hirzel, Zeitschr. f. Pharm. 1850, p. 17; Jahresb. 1850, p. 332.)

Potassio-mercuric sulphate, $3Hg''K^2(SO^4)^2.2H^2O$, is produced by dissolving 1 pt. of dry mercuric sulphate in warm sulphuric acid, adding a solution of 1 pt. potassic sulphate, digesting till the whole is dissolved, and gradually adding boiling water till a permanent cloud just begins to form. By slow cooling, it crystallises in large, colourless, monoclinic prisms. (Hirzel.)

Mercuric sulphato-iodide, $Hg''SO^4.Hg''I^2$, is produced by dissolving mercuric iodide, with aid of heat, in concentrated sulphuric acid, and separates from the solution in white confused crystals, which may be washed with alcohol, but are decomposed by water. (Souville, J. Pharm. xxvi. 174.)

Mercuric sulphato-phosphide, $2(3Hg''O.SO^3).Hg^3P$, is obtained, by passing phosphoretted hydrogen-gas into a solution of mercuric sulphate containing free sulphuric acid, as a heavy white powder, which, after drying in a vacuum, contains 4 at. water, but becomes anhydrous and yellow when gently heated. It dissolves easily in nitromuriatic acid. (H. Rose, Pogg. Ann. xl. 75.)

Mercuric sulphato-sulphide, $2Hg''SO^4.Hg''S$, discovered by Rose, is produced, by imperfect precipitation of mercuric sulphate with sulphydric acid, as a white flocculent precipitate, acquiring a yellowish tinge when dried at 100°. (Jacobsen, Pogg. Ann. lxviii. 411.)

β. *Mercurous Sulphate*, $Hg^2SO^4 = Hg^2O.SO^3$, is obtained by heating 1 pt. of mercury with 1½ pt. strong sulphuric acid, till the whole is converted into a white powder, but no longer; care must also be taken that the heat does not rise to the boiling-point of the acid, as in that case mercuric sulphate will also be formed. The mass is to be washed with cold water, as long as the water acquires a sour taste. According to Mohr, it may be obtained as a sublimate, by heating mercuric sulphate to redness in a retort. It is also precipitated as a white crystalline powder, on mixing a solution of mercurous nitrate with sulphuric acid or sulphate of sodium.

Mercurous sulphate is sparingly soluble in water, requiring 500 pts. of cold and 300 pts. of warm water to dissolve it. It separates from the solution in rhombic prisms, also from solution in boiling dilute sulphuric acid. Caustic alkalis, added in small quantity to a boiling solution of this salt, throw down a basic mercurous sulphate; when added in excess, they precipitate pure mercurous oxide.

A *mercuroso-mercuric sulphate*, $Hg^2SO^4.2Hg''SO^4$, is produced, according to Brooke, by heating mercuroso-mercuric nitrate with sulphate of sodium. It is insoluble in cold water.

Sulphates of Molybdenum.—*Molybdous sulphate*, $Mo''SO^4 = MoO.SO^3$, prepared by dissolving molybdous hydrate in sulphuric acid, forms a nearly black solution. By triturating the dry hydrate with strong sulphuric acid, a pitch-black viscid compound is obtained, which is neutral if a sufficient quantity of the hydrate has been used. Water decomposes it into a soluble acid salt and an insoluble basic salt. (Berzelius.)

Molybdic sulphate, $Mo^{iv}(SO^4)^2$, $= MoO^2.2SO^4$ is produced by dissolving molybdic hydrate in sulphuric acid, or by decomposing molybdic chloride with that acid. It is red solution, black in the dry state, or blue if dried at a higher temperature. (Berzelius).

Permolybdic sulphate, $Mo^{vi}(SO^4)^3.2H^2O = Mo^{vi}O^3.3SO^3.2H^2O$, forms (according to Berzelius) a yellow solution, which dries up to a lemon-yellow mass. According to Anderson, it may be obtained in crystals, by decomposing molybdate of barium with excess of sulphuric acid, and evaporating the filtered solution in the exsiccator. It deliquesces on exposure to the air. On boiling the solution with excess of molybdic trioxide, the liquid becomes turbid, gelatinises on cooling, and deposits a light-yellow flocculent body, probably a basic salt, somewhat soluble in water, but insoluble in alcohol.

Sulphate of Nickel, $Ni''SO^4 = Ni''O.SO^3$, is obtained by dissolving metallic nickel in dilute sulphuric acid mixed with a little nitric acid, or by dissolving the hydrate or carbonate of nickel in dilute sulphuric acid. The solution, concentrated by evaporation, yields crystals containing 6 or 7 at. water, according to the temperature at which they separate. Below 15°, the salt $NiSO^4.7H^2O$ separates in emerald-green crystals, isomorphous with sulphate of magnesium; but between 15° and 20°, emerald-green, quadratic octahedral crystals are deposited, containing $Ni''SO^4.6H^2O$, exhibiting the combinations P . oP (*fig.* 228, ii. 136); P . ½P . oP (*fig.* 229); P . ½P . oP . P∞ (*fig.* 230); P . ½P . ⅓P . oP; also P . ½P . ⅓P . oP . P∞ . ∞P∞ (*fig.* 231), and ∞P∞ . P∞ . oP . P . ½P. Length of principal axis = 1·888. Angle P : P in the terminal edges = 97° 4′; in the lateral edges = 138° 56′; ½P : ½P (terminal) = 111° 4′ (lateral) = 106° 20′. Cleavage very distinct parallel to oP, less distinct parallel to ∞P∞. The former crystals, when exposed for some days to a gentle heat, are converted into aggregates of the latter, losing their transparency at the same time; sometimes also, when broken, they exhibit in their interior aggregates of the quadratic crystals (Mitscherlich). The hexhydrated salt is moreover dimorphous, a solution kept at a temperature of 50° to 70°, depositing monoclinic crystals with 6 at. water, and isomorphous with the 6-hydrated crystals of magnesic sulphate (p. 601), cobaltous sulphate, and zinc-sulphate. These crystals gradually become opaque and bluish at ordinary temperatures. (Marignac.)

Sulphate of nickel dissolves in 3 pts. of water at 10°, but is insoluble in alcohol and in ether. The crystals effloresce in dry air, and crumble to a white powder. When heated, they give off their water, the last atom being, however, retained more strongly than the rest. The anhydrous salt is yellow, and gives off part of its acid at a red heat.

A *basic nickel-sulphate* is obtained, as a light-green insoluble powder, by imperfect precipitation of the neutral salt with potash; also (according to Tupputi) by gently heating the neutral salt.

Ammoniacal Sulphates of Nickel.—Anhydrous sulphate of nickel absorbs ammonia-gas with rise of temperature, forming the pale-violet compound, $NiSO^4.6NH^3$ (H. Rose). A warm saturated solution of nickel-sulphate in aqueous ammonia, left to cool and evaporate in a vacuum, deposits (according to Erdmann,) light-blue prismatic crystals belonging to the trimetric system, and containing $NiSO^4.4NH^3.2H^2O$. This compound is very soluble in water, and is precipitated from the solution by alcohol. The solution is decomposed by boiling.

Sulphate of Nickel and Potassium, $Ni''K^2(SO^4)^2.6H^2O$, is a light-green salt forming crystals, isomorphous with the corresponding ferrous and magnesic salts, and exhibiting the combination ∞P . [∞P2] . [∞P∞]. oP . [P∞] . +P . +2P∞ (*fig.* 296, ii. 154), also without [∞P2] and [∞P∞] (*fig.* 297). It dissolves in 9 pts. of water. The corresponding *ammonium-salt,* $Ni''(NH^4)^2(SO^4)^2.6H^2O$, dissolves in 1⅛ pt. water.

Sulphate of Nickel and Zinc, $Ni''Zn''(SO^4)^2.6H^2O$, is formed (according to Mitscherlich) by digesting sulphate of nickel with metallic zinc, and separates on evaporation; in light-green efflorescent crystals, having the form of the 6-hydrated sulphate of nickel (which form ?).

The salt $Ni''Fe''K^4(SO^4)^4.12H^2O$, and the corresponding salts containing magnesium, manganese, or zinc in place of iron, and ammonium in place of potassium, crystallise in emerald-green prisms and tables, isomorphous with the salts of like composition already described. (Vohl.)

Sulphates of Osmium.—*Osmic sulphate,* $Os^{iv}(SO^4)^2 = OsO^2.2SO^3$, is produced by dissolving sulphide of osmium in excess of nitric acid, and remains after the excess of nitric acid and the osmic tetroxide simultaneously formed have been removed by distillation, as a dark yellowish-brown syrup, showing no tendency to crystallise. The yellow aqueous solution has an astringent taste, reddens litmus strongly, and is not precipitated by alkalis.—*Osmious sulphate,* $Os''SO^4$, obtained by treating sulphide of osmium with an insufficient quantity of nitric acid, or by dissolving osmious hydrate in dilute sulphuric acid, is a yellowish-brown amorphous mass.

Sulphates of Palladium.—The *neutral sulphate,* $Pd''SO^4$, is obtained, according to Kane, by dissolving palladium in sulphuric acid mixed with a little nitric acid. The solution, evaporated to a syrup, deposits the salt on cooling, in brown irregular crystals containing 2 at. water. It has a sour and metallic taste, deliquesces in moist air, and is decomposed by a large quantity of water.—A *basic salt,* $Pd''SO^4.7Pd''O.6H^2O$, is formed when a solution of the neutral salt in a small quantity of water is diluted with a large quantity, and separates as a brown powder, which, when exposed to the air in the dry state, gradually takes up 4 at. water. (Kane.)

Sulphate of Palladammonium, $N^2H^6Pd''.SO^4$. See PALLADIUM-BASES (iv. 329).

Sulphates of Platinum.—*Platinic sulphate*, $Pt^{iv}(SO^4)^2$, is prepared by dissolving recently precipitated sulphide of platinum in fuming nitric acid, and evaporating at a gentle heat (E. Davy); or by mixing a concentrated aqueous solution of platinic chloride with sulphuric acid, and evaporating to dryness (Berzelius). The dry salt is nearly black, the solution dark-brown. It is decomposed by sal-ammoniac when evaporated to dryness therewith. (E. Davy, Phil. Trans. 1820; Schw. J. xxxi. 340.)

Bario-platinic sulphate is formed, as a precipitate insoluble in water, on mixing a solution of platinic sulphate with chloride of barium. It dissolves in boiling hydrochloric acid, and is not decomposed by alkalis. (E. Davy, *loc. cit.*)

Potassio-platinic sulphate is formed, by boiling a solution of platinic sulphate with potash, as a dark-brown precipitate, which is insoluble in water, dissolves in hydrochloric acid at the boiling heat, turns black on drying, and decomposes at a red heat. (E. Davy.)

Sodio-platinic sulphate is a similar double salt, containing 7·11 per cent. sodic sulphate, 84·16 platinum, and 8·73 water. (E. Davy.)

Platinous sulphate, $Pt''SO^4$, is obtained by saturating as olution of platinous oxide in potash with sulphuric acid, decanting the liquid, and dissolving the precipitated oxide in dilute sulphuric acid (Berzelius); also by digesting platinous chloride with strong sulphuric acid, as long as hydrochloric acid is thereby eliminated (Vauquelin). The solution is dark-brown, turns red on dilution, and leaves a black syrup when evaporated.

Respecting the *ammoniacal sulphates of platinum*, see PLATINUM-BASES (iv 675–677).

Sulphates of Potassium.—*a*. *Normal* or *Neutral Sulphate*, $K^2SO^4 = K^2O.SO^3$. *Tartarus vitriolatus. Arcanum duplicatum. Sal polychrestum Glaseri. Sal de duobus. Specificum purgans Paracelsi. Panacea holsatica. Panacea duplicata. Nitrum vitriolatum. Spiritus vitrioli coagulabilis.*—This salt occurs native, in delicate needle-shaped crystals, or as a crust, on many of the Vesuvian lavas, and is designated mineralogically as *Glaserite, Arcanite, Aphthitalite, Aphthalose*, or *Vesuvian salt*. It exists more abundantly, however, in solution in sea-water and spring-water, and in the bodies of plants and animals. It is obtained as a bye-product in several manufacturing processes, as in the preparation of nitric acid from nitrate of potassium, the acid sulphate usually obtained as a residue of this operation being converted into neutral sulphate by addition of potassic carbonate. The quantity thus produced is, however, not so great at present as formerly, in consequence of the substitution of sodic for potassic nitrate as a source of nitric acid. Sulphate of potassium is also obtained when the residue left on treating crude potash with cold water (iv. 710) is dissolved in a small quantity of boiling water. It likewise crystallises out from the mother-liquors of sea-water and salt-springs, and of the liquors obtained by lixiviating kelp and varec, when these mother-liquors are left to cool at a certain stage of the concentration (iv. 713–719). According to Payen, 300,000 kilogrammes of this salt are annually obtained in France from varec. Further, it may be formed directly by heating a solution of chloride of potassium with kieserite, $MgSO^4.H^2O$, or ordinary sulphate of magnesium, under a pressure of 10 atmospheres (Clemm, Jahresb. 1864, p. 764); and from felspar by calcining that mineral with lime and sulphate of calcium or barium. (Tilghmann, iv. 719.)

Sulphate of potassium crystallises in four-sided prisms, or double six-sided pyramids, belonging to the trimetric system (*figs.* 269–275, CRYSTALLOGRAPHY, ii. 148, 149); also in twins like *fig.* 331 (ii. 162). Cleavage parallel to $\infty\breve{P}\infty$ and $\infty\bar{P}\infty$. Axes $a : b : c = 0·7464 : 1 : 0·5727$. Angle $P : P$ (brach.) $= 131° 8'$; $\infty P : \infty P$ (macr.) $= 73° 28'$; $\infty\breve{P}2 : \infty\breve{P}2 = 112° 22'$; $\breve{P}\infty : \breve{P}\infty$ (basal) $= 59° 36'$. The salt was formerly supposed, under certain circumstances, to form crystals belonging to the hexagonal system; but these crystals are now known to consist of sodio-potassic sulphate (p. 609). The crystals of potassic sulphate are colourless, very hard, anhydrous, and unalterable in the air; they decrepitate when heated, and melt at a bright red heat. Specific gravity = 2·662 (Kopp); 2·572. (Buignet.)

Sulphate of potassium has a saline bitter taste, and is one of the least soluble of potassium-salts. According to Kopp (Ann. Ch. Pharm. xxxiv. 361), 100 pts. of water dissolve 8·36 pts. of it at 0°, and 0·1741 pt. for every degree above 0°. According to Kremers (Pogg. Ann. xcv. 120), the specific gravity of the solution varies with its strength, as follows:

Specific gravity of aqueous solution at 19·5° (specific gravity of water at 19·5° = 1).	Quantity of K^2SO^4 in 100 pts. of solution.	Quantity of K^2SO^4 in 100 pts. of water.
1·0193	2·401	2·46
1·0385	4·744	4·98
1·0568	6·968	7·49
1·0763	9·264	10·21
1·0909	10·945	12·29

A saturated solution boils at 103°. (Kremers.)

Sulphate of potassium is insoluble in potash-ley of specific gravity 1·35 (Liebig), but more soluble in the aqueous solutions of other salts (as the sulphates of sodium, magnesium, and copper) than in puro water (Pfaff, Ann. Ch. Pharm. xcix. 227). It is insoluble in absolute alcohol, but soluble in dilute spirit. According to Schiff (Ann. Ch. Pharm. cxviii. 365):

A solution (saturated at 15°) in spirit of:		Contains per cent. of K^2SO^4.
Specific gravity.	Per cent. by weight.	
1·000	0	10·4
0·986	10	3·9
0·972	20	1·46
0·958	30	0·55
0·939	40	0·21

Most of the stronger acids abstract half the potash from neutral sulphate of potassium, and convert it into the acid sulphate.

With nitric and with phosphoric acid, however, it forms definite compounds. A solution of the salt in *nitric acid*, first deposits crystals of acid sulphate and nitrate of potassium, and afterwards the compound $K^2SO^4.HNO^3$, in oblique four-sided prisms, which have a specific gravity of 2·381, melt at 150°, and are decomposed by water and by alcohol. The compound $K^2SO^4.H^3PO^4$ crystallises, on cooling, from a solution of neutral potassic sulphate in *ordinary phosphoric acid*, in six-sided prisms, which have a specific gravity of 2·296, and melt at 240°. Both compounds are decomposed by water and by alcohol. (Jacquelain, Ann. Ch. Phys. [2], lxx. 311.)

β. Acid Sulphates.—Hydro-monopotassic sulphate, $KHSO^4$ or $K^2SO^4.H^2SO^4$, commonly called *Bisulphate of potash*, occurs native as *Misenite*, in white silky fibres, in the hot tufa cavern of Miseno near Naples. It may be produced by melting 13 pts. of the neutral sulphate with 8 pts. of strong sulphuric acid, and is obtained as residue in the preparation of nitric acid by distilling 1 at. nitrate of potassium with 1 at. sulphuric acid (iv. 78). It dissolves in about half its weight of boiling water, and crystallises from a concentrated solution on cooling, in rhombic octahedrons and combinations thereof, often very much like those of native sulphur. Axes $a : b : c$ = 0·8611 : 1 : 1·9347. Angle P : P (brach.) = 103° 36′; P : P (macr.) = 88° 12′; P : P (basal) = 142° 44′; P∞ : P∞ (basal) = 132·0; ½P∞ : ½P∞ = 96° 38′. The crystals often exhibt the simple form P (like *fig.* 260, ii. 144); often also oP . P, tabular from predominance of oP, and with the above-mentioned brachydiagonal domes subordinate. They have a specific gravity of 2·163, melt at 197°; and the fused salt solidifies on cooling in large monoclinic crystals, very much like those of felspar. The salt is therefore dimorphous. At higher temperatures it gives off water and afterwards sulphuric anhydride, leaving the neutral salt. It is decomposed by alcohol and by a large quantity of water into sulphuric acid and neutral potassic sulphate. It is often used in mineral analysis, especially for the decomposition by fusion of aluminous minerals, and of niobic and tantalic compounds.

Hydro-dipotassic sulphate, $K^4H^2(SO^4)^3 = 2K^2SO^4.H^2SO^4$ (sesquisulphate of potash), crystallises from a solution of the neutral sulphate in dilute sulphuric acid, together with the preceding salt, in asbestos-like threads (Phillips, Phil. Mag. i. 429). Jacquelain succeeded only once in preparing this salt.

Hydro-tripotassic sulphate, $K^3H(SO^4)^2$, or $3K^2SO^4.H^2SO^4$, is produced, according to Marignac (Jahresb. 1856, p. 320), by dissolving hydromonopotassic sulphate in excess of water, concentrating the solution by heat, till it yields a small quantity of crystals on cooling, then concentrating the mother-liquor again, and leaving it to crystallise, and so on. The solution then deposits, first the neutral sulphate, afterwards the hydrotripotassic, and finally the hydromonopotassic salt. The hydrotripotassic salt forms six-sided tables or acute rhombohedrons, both belonging to the monoclinic system.

γ. Anhydrosulphate, $K^2S^2O^7 = K^2SO^4.SO^3 = K^2O.2SO^3$ (anhydrous bisulphate of potash), is formed, according to Jacquelain (Ann. Ch. Phys. [2] lxx. 311) by dissolving 1 at. of the neutral salt and 1½ at. sulphuric acid in water, and leaving the solution to evaporate; also when the neutral salt is heated in a platinum-crucible with half its weight of sulphuric acid, till that acid is no longer given off at a commencing red heat. It crystallises in prismatic needles, of specific gravity 2·277, which melt at 210°. These crystals, when left immersed in water for several days, gradually disappear, and the solution yields large crystals of hydromonopotassic sulphate. The anhydrosulphate dissolves very easily in hot water, and crystallises unaltered on cooling, but is decomposed by a quantity of water larger than that required to dissolve it.

8. *Double Salts.—Sodio-tripotassic sulphate*, $K^3Na(SO^4)^2$, technically called *plato-sulphate of potash*, and formerly regarded as neutral sulphate of potassium, is deposited, on cooling, from the aqueous extract of kelp, when this liquid is concentrated to commencing crystallisation, and is obtained in cakes of greater thickness, by repeatedly pouring fresh quantities of warm saturated liquor on the separated salt. Its crystallisation, especially when the temperature of the liquid has sunk to 38°, is accompanied by vivid flashes of light, which may be increased by triturating the separated salt under the liquid, or by breaking the saline crusts formed on the surface, touching the warm saturated liquid with a crystalline mass already cooled, &c. On recrystallising it, however, no light is emitted (Penny, Phil. Mag. x. 401; Jahresb. 1855, p. 332). A solution of 1 at. Na^2SO^4 and 3 at. K^2SO^4 first deposits crystals of pure potassic sulphate, and afterwards crystals of the double salt (v. Hauer, Jahresb. 1860, p. 117). The crystals of this salt belong to the hexagonal system, exhibiting the tabular combination oR . R, or prismatic ∞R . oR . +R . −R (like *fig.* 240, ii. 139). For R, the length of the principal axis is 1·284. Angle R : R (terminal) = 88° 13′; for the pyramid composed of +R and −R, angle R : R (terminal) = 131° 2′; (basal) = 112° 0′. (Mitscherlich, Pogg. Ann. lviii. 468; v. Hauer, J. pr. Chem. lxxxiii. 356; Jahresb. 1861, p. 170.—Kopp's *Krystallographie*, 2te Aufl. 1862, p. 218.)

Sodio-pentapotassic sulphate, $K^5Na(SO^4)^3$, is produced, according to Gladstone, (Chem. Soc. Qu. J. vi. 106), by fusing the neutral or acid sulphate of potassium with common salt, or the neutral sulphate with sulphate of sodium. It crystallises from the hot solution in six-sided prisms with pyramidal summits.

Strontio-potassic sulphate, $Sr''K^2(SO^4)^2$, separates, according to H. Rose, in microscopic prisms, from a solution of the strontium-salt mixed with excess of neutral potassic sulphate.

Sulphate of Rhodium, $\overset{\prime\prime\prime}{Rh}{}^2(SO^4)^3 = Rh^2O^3.3SO^3$, is prepared by dissolving precipitated rhodium-sulphide in fuming nitric acid. It is a brown powder, soluble with red colour in water. (Berzelius.)

Potassio-rhodic sulphate is formed, according to Berzelius, when finely-divided rhodium is heated to low redness with acid sulphate of potassium. The cooled mass is yellow, or rarely rose-coloured, and dissolves in water, forming a yellow solution, from which alkalis and sulphydric acid throw down only part of the rhodium.—Another *potassio-rhodic sulphate*, probably $Rh'''K(SO^4)^2$, is obtained by treating potassio-rhodic chloride with sulphurous acid, and separates from the solution as a white powder, nearly insoluble in water, and only slightly soluble in sulphuric acid.

Sulphates of Rubidium.—The *anhydrosulphate*, $Rb^2S^2O^7 = Rb^2SO^4.SO^3$, melts, like the corresponding potassium-salt, at commencing redness, and when more strongly heated, gives off sulphuric anhydride, and is converted into the neutral salt Rb^2SO^4. The latter separates from aqueous solution in large, hard, vitreous crystals, isomorphous with sulphate of potassium, and exhibiting the combination P . 2P∞. Axes, $a : b : c = 0·5723 : 1 : 0·7522$. Angle P : P (brach.) = 131° 6′; P : P (macr.) = 87° 8′; P : P (basal) = 113° 6′; ∞P : ∞P (macr.) = 73° 54′; ∞P2 : ∞P2 (macr.) = 112° 46′; P∞ : P∞ (basal) = 59° 34′. The crystals are anhydrous, permanent in the air, decrepitate and become opaque when heated.

Sulphate of rubidium forms, with *sulphate of aluminium*, an alum containing $Al'''Rb(SO^4)^2.12H^2O$; and with the *sulphates of nickel, cobalt, magnesium*, &c., hexhydrated double salts, isomorphous with the corresponding potassium-compounds. (Kirchhoff and Bunsen, Pogg. Ann. cxv. 584; Jahresb. 1861, p. 177.)

Sulphate of Ruthenium, $Ru^{iv}(SO^4)^2 = RuO^2.2SO^3$, is obtained by the action of nitric acid on the sulphide of ruthenium precipitated from the trichloride by sulphydric acid. It forms an orange-yellow solution, which, when evaporated to dryness, leaves a yellow-brown, amorphous, deliquescent mass, having a sour astringent taste. The finely-divided dry powder resembles mosaic gold. The aqueous solution yields a yellow-brown precipitate with alkalis only on heating, and is coloured blue by sulphydric acid. (Claus.)

Sulphate of Silver, $Ag^2SO^4 = Ag^2O.SO^3$. *Silver-vitriol.*—This salt is produced either by dissolving silver in boiling sulphuric acid, or by precipitating a solution of the nitrate with sulphate of sodium. It is a white inodorous powder, having a disagreeable metallic taste, melts at a rather low temperature, and decomposes at a higher temperature, leaving metallic silver. When exposed to light, it gradually turns green. It dissolves in 200 pts. of cold and 88 pts. of boiling water, and crystallises on cooling in anhydrous shining needles. According to Mitscherlich, the best crystals are obtained by slow evaporation of a solution of the salt in nitric acid. They are trimetric and isomorphous with anhydrous sulphate of sodium, exhibiting the combination $P \,.\, \infty\breve{P}\infty \,.\, \infty P \,.\, \frac{1}{3}P$. Axes, $a : b : c = 0{\cdot}4614 : 1 : 0{\cdot}8078$. Angle $P : P$ (brach.) $= 136° 20'$; $P : P$ (macr.) $= 72° 32'$; $P : P$ (basal) $= 125° 11'$. Cleavage parallel to P and $\infty\breve{P}\infty$.

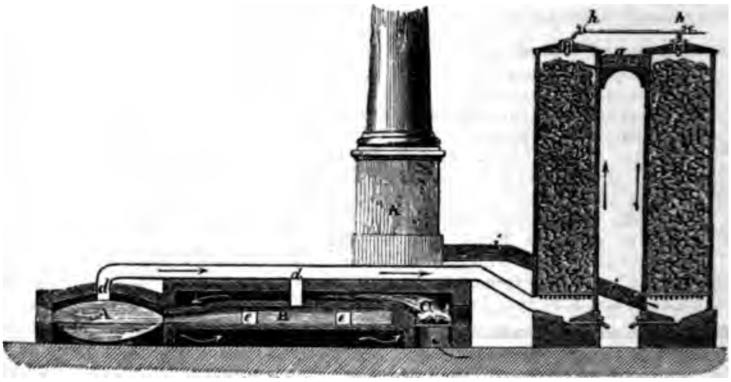
A *sulphato-sulphide of silver* is formed by digesting the sulphide with nitric acid, as a brown-yellow powder, which when boiled with excess of nitric acid, is completely converted into sulphate. Boiling water dissolves out the sulphate of silver and leaves the sulphide. (Berzelius.)

Sulphate of Argentammonium, $(NH^3Ag)^2SO^4$, is formed by saturating the dry sulphate with ammonia-gas (H. Rose). Mitscherlich obtained the compound $Ag^2SO^4.4NH^3 = [N^2H^4(NH^4)^2Ag^2]''(SO^4)$, by dissolving recently precipitated argentic sulphate in warm strong ammonia: it separated on cooling in colourless crystals, tolerably permanent in the air.

Silver-alum, $Al'''Ag(SO^4)^2.12H^2O$, has already been described.—A basic *argento-ferric sulphate*, $18(2Ag^2O.SO^3).(2Fe^2O^3.SO^3)$, is obtained, according to Lavini, by leaving a solution of argentic and ferric sulphates for some time in a closed vessel, and separates in rust-brown crystalline crusts, soluble in 100 pts. of water.

Sulphates of Sodium.—*a.* The *Normal* or *Neutral Salt*, $Na^2SO^4 = Na^2O.SO^3$. *Glauber's Salt. Sal mirabile Glauberi. Natrum sulphuricum crystallisatum.*—This salt was discovered and described in 1658 by Glauber, who prepared it from the residue obtained in the preparation of hydrochloric acid from common salt and sulphuric acid. It occurs rather abundantly in nature, either anhydrous, as *Thénardite*, crystallised in right rhombic prisms, or with 10 at. water, as Glauber's salt, in monoclinic prisms. Thénardite is found at Tarapaca in Peru, and at Espartinas near Madrid. Glauber's salt occurs in crystals, or more frequently in efflorescent crusts, at Ischl and Hallstadt in Austria; also in Hungary, Switzerland, Italy, &c.; it is abundantly deposited at the hot springs of Karlsbad; in large quantity also in a cavern in Hawaii, being formed by the action of volcanic heat and gases on salt-water; and effloresces with other salts in the limestone below the Genesee Falls, Rochester, New York; also near the Sweetwater river, Rocky Mountains. It occurs more abundantly in combination with calcic sulphate, as *glauberite* or *brongniartin* (ii. 845). Sulphate of sodium is also a constituent of seawater and of most brine springs, and exists in large quantity in many salt lakes of Russia, and in many mineral waters, as those of Karlsbad and Püllna.

FIG. 795.



Sulphate of sodium is prepared in enormous quantities by the action of sulphuric acid on common salt as a preliminary step in the manufacture of carbonate of sodium. The operation is performed in a reverberatory furnace connected with an apparatus for condensing the hydrochloric acid. One of the best forms of furnace is represented in *fig.* 795, the arrangement of the flues being, however, somewhat different.

A, the smaller of the two compartments which compose the furnace, is of cast iron;

In this (the *decomposer*) from 5 to 6 cwt. of common salt is introduced, and an equal weight of sulphuric acid (of specific gravity 1·6) is gradually mixed with it, a gentle heat being applied to the outside; enormous volumes of hydrochloric acid are disengaged, and pass off by the flue *d*, to the condensing towers E and F. These towers are filled with fragments of coke or stone, over which a continuous stream of water is caused to trickle slowly from *h h*. A steady current of air is drawn through the furnace and condensing towers, by connecting the first tower with the second, as shown at *g*, and the second tower with the main chimney (E) of the works. In the first bed of the furnace, about half the chlorine is expelled as hydrochloric acid from the common salt, and the pasty mass thence resulting is pushed through a door into the roaster, or second division (B) of the furnace. In this state it consists of a mixture of acid sodic sulphate and undecomposed sodic chloride:

$$2NaCl + H^2SO^4 = NaCl + NaHSO^4 + HCl.$$

In the second stage, a higher temperature is required, the acid sulphate then reacting on the unchanged chloride, in such a manner as to convert the whole of the sodium in to normal sulphate:

$$NaCl + NaHSO^4 = HCl + Na^2SO^4.$$

The fused sulphate of sodium thus obtained is called salt-cake. The hydrochloric acid gas, as it is liberated from B, passes through the flue *d*, and is carried on to the condensing towers. Heat is applied to the outside of the roaster B; the smoke and products of combustion circulate in separate flues round the chamber, in the direction indicated by the arrows, but never come into contact with the salt-cake in B. (Miller's *Elements of Chemistry*, 3rd edition, part ii. p. 420.)

For further details, see Richardson and Watts's *Chemical Technology*, vol. i. part. iii. pp. 204—215, and part v. pp. 235—244.

Sulphate of sodium is likewise obtained as a residue in many chemical operations as: (*a*) in the preparation of nitric acid with sulphuric acid and Chilè saltpetre; (*b*) of, sal-ammoniac from sulphate of ammonium and chloride of sodium; (*c*) of *magnesia alba* from sulphate of magnesium and carbonate of sodium.—(*d*) Considerable quantities are also obtained from the panstone and mother-liquors in the preparation of common salt from sea-water and salt-springs (p. 333). The panstone, which often consists mainly of a mixture of common salt and anhydrous calcio-sodic sulphate, is lixiviated with water, which dissolves out the sulphate of sodium; the non-saturated solutions are poured upon fresh panstone, and the saturated solutions into large receivers, in which the sulphate of sodium crystallises out in winter. From the mother-liquor of brine-springs and of sea-water, sulphate of sodium is separated by fractional crystallisation, the liquor being exposed during winter to a freezing temperature. The sulphate of sodium partly exists in these mother-liquors ready-formed, and is partly produced by the mutual action of the magnesic sulphate and sodic chloride contained in them, so that the mother-liquor left after the separation of the sodic sulphate contains chiefly chloride of magnesium. The crude salt is dissolved in water at 33°, and separates from the solution on cooling in large tolerably pure crystals (Richardson and Watts's *Chemical Technology*, vol. i. part iii. pp. 157, 545).—*e*. By the decomposition of ferrous sulphate with chloride of sodium, a mixture of these two salts depositing sulphate of sodium when exposed to a winter temperature. It may also be formed by heating iron-pyrites or green vitriol with common salt in a reverberatory furnace, hydrochloric acid then going off, and the iron being partly volatilised as chloride, partly remaining in the form of ferric oxide. At Fahlun, in Sweden, Glauber's salt is obtained from the mine-water, and from the mother-liquor of green vitriol, by mixing these liquids with the requisite quantity of common salt, evaporating to dryness, igniting, and dissolving the residue in hot water.

Sulphate of sodium is obtained, as an anhydrous mass, by leaving ordinary Glauber's salt (the decahydrate) to effloresce, or by heating it to redness, and in anhydrous crystals by heating a solution saturated at 33° to 40°, some degrees higher; according to Mitscherlich, it separates even at 40°. These crystals, which have the same form as thénardite, are rhombic octahedrons ismorphous with sulphate of silver, and with the selenates of sodium and silver, and exhibit the combination $P . \frac{1}{3}P . \infty P . \infty\breve{P}\infty$. Axes $a:b:c = 0{\cdot}4734 : 1 : 0{\cdot}8005$. Angle P : P (brach.) = 135° 41′; P : P (macr.) = 74° 18′; P : P (basal) = 123·43°. Cleavage parallel to P. and $\infty\breve{P}\infty$. The salt melts at a strong red heat to a thin liquid, and solidifies on cooling to a transparent crystalline mass. Specific gravity of the crystals = 2·73 (Cordier); 2·645 (Thomson); of the solid fused salt = 2·693 (Karsten; Schröder). By ignition with charcoal, it is converted into monosulphide of sodium.

Sulphate of sodium crystallises from solution at ordinary temperatures, in large, colourless, striated, monoclinic prisms, containing $Na^2SO^4.10H^2O$, and isomorphous with chromate and selenate of sodium containing corresponding quantities of water. Axes $a : b : c = 0·8962 : 1 : 1·109$. Angle $b : c = 72° 15'$; ∞P : ∞P (orthod.) = 93° 29′; [P∞] : [P∞] (clinod.) = 80° 38′; [2P∞] : [2P∞] (clinod.) = 45° 58′; +P∞ : c = 49° 50′; +½P∞ : c = 75° 19′; − ½P : c = 47° 56′; oP : ∞P = 77° 56′. The ordinary combination is ∞P . ∞P∞ . oP . [P∞]. +P. +P∞. The crystals are almost always prismatically elongated in the direction of the orthodiagonal, and cleave very distinctly parallel to ∞P∞. They effloresce readily on exposure to the air, melt in their water of crystallisation at 33°, and give off the whole of it below 100°.

The salt has a bitter and cooling taste, and is used as a purgative. 100 pts. of water dissolve 12 pts. of it at 0°; 48 pts. at 18°; 100 pts. at 25°; 322·6 pts. at 33°; 263 pts. at 50° (Gay-Lussac), and 244 pts. at 100° (Brandes and Firnhaber). Hence it appears that there is a maximum of solubility at about 34°.

When a solution saturated at the point of greatest solubility is left to cool in a closed vessel and at perfect rest, it remains supersaturated at ordinary temperatures, and does not crystallise; but on agitating it in contact with the air, or dropping a crystal of the salt into it, the whole solidifies, with rise of temperature, to a mass of crystals of ordinary Glauber's salt. If, however, the supersaturated solution be cooled below 12°, without agitation, crystals are sometimes formed containing 7 at. water and much harder than the decahydrated crystals. If now the temperature be again raised above 15°, or the crystals touched, they become milk-white, and are converted, with considerable rise of temperature, into a mixture of the anhydrous and the decahydrated salt. (Ziz; Faraday; Löwel.)

The heptahydrated salt, $Na^2SO^4.7H^2O$, crystallises in rhombic prisms, ∞P . ∞$\bar{P}$3 . ∞$\breve{P}$∞, terminated by the faces, $\breve{P}$∞ . ⅓$\breve{P}$∞. Axes $a : b : c = 0·955 : 1 : 0·966$. ∞P : ∞P (macr.) = 87° 20′ : ∞$\bar{P}$3 : ∞$\bar{P}$3 = 35° 18′; $\breve{P}$∞ : $\breve{P}$∞ (basal) = 88° 0′; ⅓P∞ : ⅓P∞ (basal) = 35° 40′.

According to Löwel (Ann. Ch. Phys. [3], xlix. 32; Jahresb. 1856, p. 321), sulphate of sodium may exist in solution in three different states—viz., as anhydrous salt, or as the ordinary decahydrate, or as the heptahydrate. When the ordinary decahydrated crystals are melted in their water of crystallisation, then heated till the liquid boils, and the vessel immediately closed, a crystalline powder of the anhydrous salt is deposited. If the liquid be frequently agitated as it cools, the anhydrous salt dissolves more and more, till the temperature has fallen to 18°. On further cooling, crystals of the salt $Na^2SO^4.7H^2O$ are deposited on the still undissolved residue, and below 18°, the anhydrous salt is gradually but completely converted into the heptahydrate. The solutions of the anhydrous sulphate remain as such at ordinary temperatures only in closed vessels; in contact with the air, or a crystal of Glauber's salt, they immediately deposit crystals of the decahydrated salt. The solubility of the anhydrous salt diminishes as the temperature rises; but that of the ordinary decahydrate increases up to about 34°, at which temperature it is converted into the anhydrous salt. At 34°, the decahydrated crystals gradually melt in their water of crystallisation. As long as the saturated liquid remains in contact with a large excess of the unaltered crystals, it retains an amount of salt corresponding to that in a solution of the decahydrated salt saturated at 34°—that is to say, 55 pts. of anhydrous salt to 100 pts. water. If, however, the fusion be continued further, the anhydrous salt begins to separate; and when all the crystals are fused, the solution ultimately contains 49·53 pts. of anhydrous salt to 100 pts. water, an amount corresponding to that of a solution of the anhydrous salt saturated at 34°. Hence the apparent maximum in the solubility of sodic sulphate at 34°, arises from the fact that the salt, under ordinary circumstances, dissolves in water up to the temperature of 34°, as $Na^2SO^4.10H^2O$, the solubility of which increases with the temperature; but above 34°, it dissolves as anhydrous salt, the solubility of which diminishes as the temperature rises up to 103·7°, the boiling-point of the saturated solution. (Löwel.)

Saturated solutions of the salt $Na^2SO^4.7H^2O$ are obtained, for higher temperatures, by removing, at a lower temperature, a portion of the mother-liquor which covers the crystals, and then warming the crystals with the rest of the liquid. When a liquid containing an excess of the crystals of this heptahydrate is heated to 27°, these crystals behave just like those of the decahydrate at 34°—that is to say, they melt, and the liquid deposits the anhydrous salt. (Löwel.)

The following table exhibits the variations of solubility of anhydrous sodic sulphate, and of the two hydrates; in the two latter cases, also, the quantity of anhydrous salt equivalent to the hydrated salt dissolved at each temperature is given:—

Quantities of Sodic Sulphate dissolved in 100 pts. of Water in the state of Saturated Solution.

Temperature.	Na^2SO^4, Anhydrous.	$Na^2SO^4 + 10H^2O$.		$Na^2SO^4 + 7H^2O$.	
		Anhydrous.	Hydrate.	Anhydrous.	Hydrate.
0°C.	. .	5·02	12·16	19·62	44·84
10	. .	9·00	23·04	30·49	78·90
15	. .	13·20	35·96	37·43	105·79
18	52·25	16·80	48·41	41·63	124·59
20	52·76	19·40	58·35	44·73	140·01
25	51·53	28·00	98·48	52·94	188·46
26	51·31	30·00	109·81	54·07	202·61
30	50·37	40·00	184·09		
33	49·71	50·76	323·13		
34	49·53	55·00	412·22		
40·15	48·78				
50·40	46·82				
59·79	45·42				
70·61	44·35				
84·42	42·96				
103·17	42·65				

Sulphate of sodium is insoluble in alcohol, but somewhat soluble in dilute spirit; strong alcohol heated with the ordinary crystals, abstracts part of their water of crystallisation. According to Schiff (Ann. Ch. Pharm. cxviii. 365):

A solution (saturated at 15°) in alcohol of:		Contains per cent. of
Specific gravity.	Per cent by weight.	$Na^2SO^4.10H^2O$.
1·000	0	25·6
0·976	10	14·35
0·972	20	5·6
0·939	40	1·3

Alcohol precipitates it from the cold aqueous solution.—[On the solubility of sodic sulphate in various liquids, see further, Storer's *Dictionary of Solubilities*, iii. 623—628.]

Strong hydrochloric acid poured upon crystallised Glauber's salt, produces considerable depression of temperature.

β. Acid Sulphates of Sodium.—Hydro-monosodic sulphate, $NaHSO^4$ or $Na^2SO^4.H^2SO^4$, commonly called *hydrated bisulphate of soda*, is obtained, in large transparent triclinic crystals, by dissolving equivalent quantities of the neutral sulphate and sulphuric acid in water, and evaporating by heat. From a solution saturated at the boiling heat, it separates on cooling in oblique rhombic prisms containing 2 at. water, according to Mitscherlich, 3 at. according to Wittstein. The crystals, when exposed to the air, graduallly, absorb water without deliquescing, and are resolved into the neutral salt and free sulphuric acid. The same decomposition takes places on dissolving them in 4 pts. of hot water or pouring alcohol upon them.

Hydro-trisodic sulphate, $Na^3H(SO^4)^2$, is obtained, according to Mitscherlich, when the neutral sulphate is treated with half the quantity of sulphuric acid required to convert it into the preceding salts; it crystallises by evaporation in beautiful oblique rhombic prisms. H. Rose always obtained it from a solution of hydromonosodic sulphate, and in one preparation it was deposited in small crystals with a somewhat different amount of water. Its aqueous solution always yields crystals of neutral sodic sulphate with 2½ at. water (H. Rose). Mitscherlich sometimes also obtained crystals containing $Na^3H(SO^4)^2$.

The *anhydrosulphate*, $Na^2S^2O^7 = Na^2SO^4.SO^3 = Na^2O.2SO^3$, or *anhydrous bisulphate of soda*, is obtained by covering 1 at. of the dry neutral sulphate with 1 at. sulphuric acid, and heating till the mass fuses tranquilly at a low red heat. When heated to full redness, it gives off sulphuric anhydride (p. 569).

Sulphate of Strontium, $Sr''SO^4. = SrO.SO^3$, occurs native as cœlestin, sometimes in large trimetric crystals, sometimes sparry or fibrous (i. 1069.) Manross, by fusing sulphate of potassium with excess of chloride of strontium, obtained sulphate of strontium in crystals having the form and specific gravity of cœlestin. By precipitating a soluble strontium-salt with sulphuric acid, it is obtained as a white powder which, according to Fresenius, is soluble in 6,895 pts. of cold and 9,638 pts. of boiling water, but much less soluble in water containing hydrochloric or sulphuric acid, of which it requires 11,800 parts. The aqueous solution is used as a reagent for distinguishing barium from strontium (p. 436). According to H. Rose, sulphate of strontium dissolves very perceptibly in hydrochloric acid at ordinary temperatures. Water containing common salt dissolves it slowly but completely. Virck (Chem. Centr. 1862, p. 402) has determined the solubility of sulphate of strontium in certain saline solutions with the following results:—

Quantity of salt in solution.	Quantity of $SrSO^4$ dissolved.	Quantity of salt in solution.	Quantity of $SrSO^4$ dissolved.
NaCl 22·17	0·1811	$MgCl^2$ 13·63	0·2419
„ 15·54	0·2186	„ 4·03	0·2057
„ 8·44	0·1653	„ 1·59	0·1986
KCl 18·08	0·2513	$CaCl^2$ 33·70	0·1706
„ 12·54	0·1933	„ 16·51	0·1853
„ 8·22	0·1925	„ 8·67	0·1756

Sulphate of strontium melts to a vitreous mass at a strong red heat, and is reduced on charcoal before the blowpipe to sulphide of strontium. With an equivalent quantity of sodic carbonate, it forms an easily fusible mass, which, on cooling, becomes opaque, and like mother-of-pearl.

Sulphate of Tellurium, $Te^{iv}(SO^4)^2 = TeO^2.2SO^3$?—When pulverised tellurium is triturated to a thin paste with strong sulphuric acid, and the mass gently heated, it assumes a fine purple-red colour, arising, according to Magnus, from the solution of the tellurium as such, and not in the oxidised state. The purple colour remains as long as there is any liquid left, whilst the undissolved portion of the tellurium becomes oxidised at the expense of the sulphuric acid, and disappears as soon as all the acid is decomposed, the whole being then converted into a white mass. If this mass be gently heated till the excess of acid is just driven off, there remains a white, earthy, amorphous substance, which produces a sense of dryness on the tongue, and after a while a metallic taste. When heated it melts, gives off sulphuric anhydride, and leaves a yellow liquid, which solidifies on cooling to a transparent vitreous mass, consisting of a basic salt, which, when heated in an open crucible, gives off its sulphuric acid, and leaves opaque tellurous oxide. Sulphate of tellurium dissolves in warm hydrochloric or nitric acid, and crystallises therefrom in granules on cooling. Water decomposes it, dissolving out sulphuric acid with a small quantity of tellurium, and separating tellurous oxide (Magnus, Pogg. Ann. x. 491). See further Gmelin's *Handbook*, iv. 406.

Sulphate of Terbium, $3Tb''SO^4.8H^2O$, is isomorphous with sulphate of didymium (Delafontaine, Jahresb. 1864, p. 198; 1865, p. 179). According to Mosander, it effloresces at 50°; Delafontaine, however, only once observed an imperfectly crystallised specimen to effloresce completely at ordinary temperatures. (See TERBIUM.)

Sulphates of Thallium.—*a. Thallious sulphate*, $Tl^2SO^4 = Tl^2O.SO^3$, is obtained by evaporating a solution of the chloride or nitrate with sulphuric acid (Lamy), or by heating metallic thallium with sulphuric acid (Crookes). It is soluble in 21·1 pts. of water at 15° and in 5·4 pts. at 100° (Crookes), and crystallises from the solution in anhydrous rhombic prisms, isomorphous with sulphate of potassium, and exhibiting the combination $\infty\breve{P}\infty \,.\, \infty\breve{P}2 \,.\, \infty P \,.\, \infty\bar{P}\infty \,.\, P \,.\, \breve{P}\infty$; the crystals are prismatically elongated in the direction of the principal axis, and the faces $\infty\breve{P}\infty$ greatly predominate (v. Lang, Phil. Mag. [4] xxv. 348). In presence of sulphate of ammonium, it separates in long striated crystals resembling sulphocyanate of potassium. (Crookes, Chem. News, viii. 243.)

Thallious sulphate forms, with sulphate of potassium, the salt, $TlAl'''(SO^4)^2.12H^2O$, isomorphous with common alum (Lamy); and with the sulphates of magnesium, nickel, &c., double salts containing 6 at. water, and isomorphous with potassio-magnesic sulphate, &c. (G. Werther, Bull. Soc. Chim. [2] ii. 272; Jahresb. 1864, p. 248).—The *nickel-salt*, $Tl^2Ni''(SO^4)^2.6H^2O$, separates from a solution containing a slight excess of nickel-sulphate, in green prisms, which are permanent in the air, give off their water at 120°, and decompose at a red heat.—The *ferrous salt*, $Tl^2Fe''(SO^4)^2.6H^2O$, obtained in like manner, is pale-green; the *zinc-salt*, $Tl^2Zn''(SO^4)^2.6H^2O$, is colourless, and has a glassy lustre; the magnesium-salt, $Tl^2Mg''(SO^4)^2.6H^2O$, resembles it, but is more soluble.

β. Thallic sulphate, $\overset{'''}{Tl}{}^2(SO^4)^3.7H^2O = \overset{'''}{Tl}{}^2O^3.3SO^3.7H^2O$, separates by evaporation from a solution of thallic oxide in dilute sulphuric acid, in thin colourless laminæ, which are decomposed by water, even in the cold, with separation of brown thallic oxide. It gives off 6 at. water at 220°, and is reduced at a stronger heat to thallious sulphate. (Strecker, Ann. Ch. Pharm. cxxxv. 207.)

According to Willm (Ann. Ch. Phys. [4] ix. 5; Jahresb. 1865, p. 253), a solution of thallic oxide in moderately concentrated sulphuric acid, prepared with aid of heat, first deposits slender needles of the basic salt, $\mathrm{Tl^2O^3.2SO^3.5H^2O}$; afterwards a *thalloso-thallic sulphate*, in transparent prismatic crystals, together with an amorphous pulverulent salt containing $\mathrm{Tl^2O^3.2SO^3.3H^2O}$. A solution of thallious sulphate heated with baric or plumbic peroxide and sulphuric acid, then filtered and concentrated by evaporation, deposits crystals of anhydrous thallic sulphate, $\mathrm{Tl^2O^3.3SO^3}$. (Willm.)

Potassio-thallic sulphate, $\overset{'''}{\mathrm{Tl}}{}^2\mathrm{K^4(SO^4)^5} = \overset{''}{\mathrm{Tl}}{}^2\mathrm{(SO^4)^2.2K^2SO^4}$, separates, on mixing a solution of the preceding salt with a strong solution of potassic sulphate, as a hard, colourless, crystalline crust, which is coloured brown on the surface by water, and is but slightly soluble in dilute sulphuric acid.—*Sodio-thallic sulphate*, $\mathrm{Tl\,Na(SO^4)^2}$, is formed in like manner, and separates in colourless needles. (Strecker.)

Sulphate of Thornium, $\mathrm{Th^{iv}(SO^4)^2 = ThO^2.2SO^3}$.*—Obtained as a white powder by dissolving thorina in strong sulphuric acid and expelling the excess of acid by evaporation (Berzelius). Delafontaine (N. Arch. Ph. Nat. xviii. 343; Jahresb. 1863, p. 197) prepares it by mixing finely pulverised thorite or orangite with strong sulphuric acid to a semi-fluid paste (the mass becoming strongly heated, and part of the excess of acid volatilising), and heating the residue to 400°—500°, as long as acid fumes are evolved; then gradually introducing the dry and cooled mass into cold water, with constant stirring, and heating the filtered solution to 100°. The sulphate of thorinum then separates, and may be purified by repeated solution in cold water and precipitation by heat.

Sulphate of thorinum thus obtained is a heavy white curdy precipitate, made up of interlaced needles, and consisting, according to Delafontaine, of $\mathrm{2Th^{iv}(SO^4)^2.9H^2O}$. By slow evaporation of an aqueous solution at ordinary temperatures (10°—15°), a salt separates containing double this amount of water, viz., $\mathrm{Th^{iv}(SO^4)^2.9H^2O}$ (Delafontaine. Chydenius, Pogg. Ann. cxix. 48; Jahresb. 1863, p. 196). Berzelius, by spontaneous evaporation of a solution containing a little free sulphuric acid, obtained a hydrate containing 10 at. water, 6 at. of which were given off at a somewhat higher temperature, leaving the salt $\mathrm{Th^{iv}(SO^4)^2.4H^2O}$, which also separated from the solution on evaporation at higher temperatures. These two hydrates were probably the same as those above mentioned, containing 9 and 4½ at. water.

The hydrate, $\mathrm{Th(SO^4)^2.9H^2O}$, crystallises, according to Chydenius, in translucent, efflorescent, monoclinic prisms, exhibiting the combination $\infty P \,.\, [P\infty] \,.\, \infty P\infty \,.\, [\infty P\infty] \,.\, oP$. Axes, $a : b : c = 1 : 0{\cdot}5981 : 0{\cdot}6584$. Angle $b : c = 81° 50'$; $\infty P \,.\, \infty P$ (clinod.) $= 118° 50'$; $[P\infty] : [P\infty]$ (over the pole) $= 149° 25'$. Delafontaine, by leaving the salt precipitated from a hot solution, in contact with a quantity of water not sufficient to dissolve it, obtained six or eight-sided, pointed, monoclinic crystals, the composition of which is not stated, but which, according to Marignac's determinations, exhibit the same faces as those just described, with addition of $[8P\infty]$ and $[\infty P\infty]$ and nearly the same value of the angle $\infty P : \infty P$, viz. 119° 0'; also $oP : \infty P\infty = 98° 20'$; $\infty P : oP = 97° 6'$; $[P\infty] : oP = 124° 28'$; $[6P\infty] : oP = 96° 27'$; $[\infty P\infty] : oP = 94° 51'$. Hence they were probably also $\mathrm{Th(SO^4)^2.9H^2O}$.

A slightly acidulated aqueous solution of sulphate of thorinum yields, when boiled, a flocculent precipitate which redissolves on cooling, and contains $\mathrm{Th(SO^4)^2.3H^2O}$, or from somewhat dilute solutions, $\mathrm{Th(SO^4)^2.H^2O}$. The solution, evaporated at 25°, yields without formation of crystals, a white saline mass consisting of $\mathrm{Th(SO^4)^2.2H^2O}$. The 9-hydrated salt gives up half its water at 100°, and the rest at a stronger heat (at 400° to 450°, according to Delafontaine). The anhydrous salt hisses when dissolved in water (Chydenius). The salt is insoluble in alcohol, and gives off all its acid at a red heat (Berzelius).—A *basic salt* is obtained on adding ammonia to the solution of the neutral salt as long as any precipitate is formed.

Potassio-thorinic sulphate, $\mathrm{Th^{iv}K^4(SO^4)^4.2H^2O = Th^{iv}(SO^4)^2.2K^2SO^4.2H^2O}$, separates, according to Berzelius, as a crystalline powder, when a crust of potassic sulphate is suspended in a solution of thorinic sulphate. It is easily soluble in water, insoluble in alcohol and in sulphate of potassium. From a boiling aqueous solution, it crystallises on cooling in rectangular prisms, which give off their water at a gentle heat, but without disintegrating (Berzelius). According to Chydenius, the salt, $\mathrm{Th^{iv}K^8(SO^4)^6.2H^2O}$, separates in slender crystals when solid sulphate of potassium is immersed in a solution of thorinic sulphate at 60°—70°.

Sulphates of Tin.—*Stannic sulphate*, $\mathrm{Sn^{iv}(SO^4)^2 = Sn^{iv}O^2.2SO^3}$, is formed by dissolving stannic hydrate in sulphuric acid, or by heating tin with excess of the acid. It forms an acid uncrystallisable syrup.

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* Th = 137.

Stannous sulphate, $Sn''SO^4 = Sn''O.SO^3$, is obtained, by heating an excess of tin with concentrated or slightly diluted sulphuric acid, as a saline mass, which dissolves with brown colour in boiling water, and separates in needle-shaped crystals on cooling; also in nacreous laminar crystals, by dissolving stannous hydrate in warm dilute sulphuric acid; and as a crystalline precipitate, by adding sulphuric acid to a concentrated solution of stannous chloride. The anhydrous salt is obtained by distilling stannous sulphide with mercuric oxide. It bears a red heat without decomposition, whereas the hydrated salt when ignited leaves a residue of stannic oxide. Stannous sulphate dissolves very easily in water, but the solution, after some time, deposits a white basic salt.

Potassio-stannous sulphate separates, on mixing a solution of stannous sulphate with sulphate of potassium in fine silky needles, containing $\acute{S}nK^2(SO^4)^2$, or $Sn''K^2(SO^4)^2$ (Marignac). A mixture of hot concentrated solutions of stannous chloride and sulphate of potassium, deposits the compound $4Sn''K^2(SO^4)^2.Sn''Cl^2$, in small, shining, hexagonal crystals, which may be recrystallised without decomposition. (Marignac.)

Sulphates of Titanium.—*Titanic sulphate*, $Ti^{iv}(SO^4)^2 = Ti^{iv}O^2.2SO^3$, is prepared by digesting finely pulverised titanic oxide with sulphuric acid diluted with half its weight of water till all the water is driven off. On expelling the excess of acid by a stronger heat, titanic sulphate remains as a saline mass, which dissolves completely in lukewarm water; the diluted solution, however, deposits titanic oxide when boiled (H. Rose). From a solution of acid potassic titanate in hydrochloric acid, sulphuric acid throws down a compound consisting of $9TiO^2.SO^3.9H^2O$ (H. Rose).—*Potassio-titanic sulphate*, $Ti^{iv}K^2(SO^4)^3$, is obtained, according to Warren (Jahresb. 1857, p. 175), in small sparingly soluble crystals, by fusing titanic oxide with acid sulphate of potassium, digesting the resulting vitreous mass with strong sulphuric acid, expelling the greater part of the latter by a gentle heat, and dissolving out the excess of acid potassic sulphate with water.

Titanous sulphate, $Ti^2O^3.3SO^3$, according to Ebelmen, is formed by dissolving trichloride of titanium in sulphuric acid, and separates on evaporating the solution in a vacuum over lime, in violet, deliquescent, crystalline masses. Its solution, when boiled, deposits titanic oxide.

Sulphate of Tungsten separates, on dropping a solution of alkaline tungstate into dilute sulphuric acid, as a heavy white precipitate, soluble in pure water.

Sulphates of Uranium.—*Uranic sulphate*, $U^2O^3.SO^3$, or *Sulphate of Uranyl*, $(U^2O^2)''SO^4$, is obtained by dissolving uranoso-uranic oxide in strong sulphuric acid, diluting the solution with water, and oxidising with nitric acid; also by decomposing a solution of uranic nitrate with sulphuric acid, expelling the excess of acid by heat, dissolving the residue in water, evaporating the solution to a syrup, and leaving it to crystallise. It forms small lemon-yellow prisms containing 3 at. water (Berzelius; Péligot); 3½ at. (Ebelmen). According to Berzelius, the salts $U^2O^3.2SO^3$ and $U^2O^3.3SO^3$, are obtained by dissolving the monosulphate in sulphuric acid; but Péligot denies their existence (see URANIUM).—Uranic sulphates of various composition, called *uranium-ochre* and *uranium-vitriol*, are found in small flattened monoclinic crystals, of a bright emerald-green colour, near Joachimsthal in Bohemia, also at Johanngeorgenstadt. (Rammelsberg's *Mineralchemie*, p. 279.)

Potassio-uranic sulphate, $(U^2O^2)''K^2(SO^4)^2.2H^2O$, forms lemon-yellow crystalline crusts, very soluble in water, and becoming anhydrous at 100°.—*Ammonio-uranic sulphate*, of similar composition, forms sparingly soluble, lemon-yellow prisms. There is also a crystalline *sodio-uranic sulphate*.—Basic *cupro-uranic sulphates*, called *uranium-green*, are found at Joachimsthal. (Rammelsberg's *Mineralchemie*, p. 295.)

Uranous sulphate, $U''SO^4 = U''O.SO^3$, may be prepared by dissolving uranoso-uranic oxide in hot oil of vitriol, diluting with water, and evaporating in a vacuum; or by dissolving hydrated uranous oxide in dilute sulphuric acid; or by decomposing a concentrated solution of uranous chloride with sulphuric acid. It crystallises with 2 and with 4 at. water.—A *dibasic uranous sulphate*, $U''SO^4.U''O.3H^2O$, is obtained by treating the normal salt with a large quantity of water; by exposing the alcoholic solution of that salt to the sun's rays; by careful addition of ammonia to its aqueous solution; and by boiling that solution with green uranoso-uranic oxide. It forms a light-green powder having a silky lustre.

Ammonio-uranous sulphate, $U''(NH^4)^2(SO^4)^2$, forms easily soluble, dark-green, warty groups of crystals: its solution, when heated, deposits a basic sulphate.

Potassio-uranic sulphate, $\acute{U}^2K^2(SO^4)^2.H^2O$, forms green, slightly soluble saline crusts.

Uranoso-uranic sulphate, $U''(U^2O^2)''(SO^4)^2$, obtained by dissolving uranoso-uranic oxide in warm oil of vitriol, and evaporating the excess of acid by heat, forms a light-green, soluble mass, which at a red heat gives off sulphurous anhydride, and is converted into uranic sulphite (Ebelmen, (Ann. Ch. Phys. v. 189). On the sulphates of uranium, see further Gmelin's *Handbook*, iv. 174.)

Sulphates of Vanadium.—*Vanadi sulphate*, $Vd^{vi}(SO^4)^3 = VdO^3.3SO^3$, is produced by dissolving vanadic oxide in hot sulphuric acid diluted with half its weight of water, and evaporating the excess of acid at as low a temperature as possible. It forms small red-brown crystalline scales, quickly deliquescing to a rusty-brown syrup, which is not rendered turbid either by water or by alcohol. The aqueous solution becomes turbid on boiling, and the liquid separated from the precipitate contains an *acid salt*, which dries up to a red syrup. A *basic salt*, $VdO^3.2SO^3$, formed by dissolving neutral vanadious sulphate in nitric acid, forms a red, deliquescent, soluble, saline mass (Berzelius). *Potassio-vanadic sulphate*, $Vd^{vi}K^2(SO^4)^4$, separates from a solution of potassic vanadate mixed with a little sulphuric acid, and left to evaporate, in yellow grains, composed of microscopic crystals. It is slightly soluble in water, insoluble in alcohol. (Berzelius.)

Vanadious sulphate, $Vd^{iv}(SO^4)^2 = VdO^2.2SO^3$, is prepared by dissolving the di- or tri-oxide of vanadium, obtained by igniting vanadate of ammonium, in sulphuric acid, and passing sulphurous acid gas through the solution, or heating it with oxalic acid, to complete the reduction of the vanadic tri-oxide. The solution, when evaporated, yields sky-blue crystals, probably consisting of an acid vanadious sulphate, which, when purified by washing with absolute alcohol, gradually swells up, and is converted into a loose sky-blue powder, consisting of the neutral salt. This salt, after being washed with alcohol, and dried over oil of vitriol, may be obtained in the crystalline form by allowing it to deliquesce, and then leaving it for some time in a dry atmosphere. It usually crystallises in groups of prisms, but sometimes in separate, short, rhombic prisms, having a fine blue colour, and consisting of $Vd^{iv}(SO^4)^2.4H^2O$. It dissolves very slowly in cold water, and when ignited, leaves vanadic tri-oxide (Berzelius). A *basic salt* is produced, according to Berzelius, by digesting a strong solution of the neutral sulphate with vanadious hydrate. It dries up to a blue transparent mass, which gives off water and turns brown at 100°. *Potassio-vanadious sulphate*, $Vd^{iv}K^2(SO^4)^3$, is a light blue gummy mass.

Sulphates of Yttrium. The *neutral sulphate*, $Y''SO^4$, crystallises very easily in small four- or six-sided, colourless, or faintly rose-coloured prisms, which do not effloresce, but remain transparent, even at 80°, but at higher temperatures give off water and become milk-white; they dissolve very slowly in water (Berzelius). A solution of yttria in sulphuric acid saturated in the cold, becomes turbid at 30°—40°, from separation of the sulphate, and at the boiling heat the whole is precipitated as a crystalline powder, containing $2Y''SO^4.5H^2O$; it has a faint reddish-colour, which it loses at 180°, together with its water of crystallisation. The anhydrous salt dissolves easily in cold water (Popp, Ann. Ch. Pharm. cxxxi. 179; Jahresb. 1864, p. 203). By evaporation over oil of vitriol at 6°—10°, crystalline crusts are obtained, consisting of $3Y''SO^4.8H^2O$, isomorphous with the corresponding hydrated sulphates of cadmium and didymium (Popp; Delafontaine, Jahresb. 1864, p. 198.) The anhydrous salt gives off $\frac{2}{3}$ of its sulphuric anhydride at a red heat, leaving the tribasic salt $3YO.SO^3 = Y''SO^4.2YO$; and by very strong and prolonged ignition, the whole of the sulphuric anhydride may be expelled, leaving pure yttria. The basic salt is likewise obtained by precipitating the neutral salt with ammonia. (Berzelius.)

Potassio-yttric sulphate, $Y''K^2(SO^4)^2$, is obtained, by evaporation of the solution of its component salts, as white crystalline crust (Berzelius); or by covering the solution with a layer of alcohol, in crystals, which, on exposure to the air, give off about 6 per cent. of water (Popp). The salt dissolves in 16 pts. of cold water, and in 10 pts. of a solution of potassic sulphate (Berzelius). The aqueous solution saturated in the cold, deposits sulphate of yttrium when heated. (Popp.)

Sulphate of yttrium may be combined by fusion with sulphate of sodium, but does not unite with sulphate of *magnesium*. (Popp.)

Sulphates of Zinc.—The *normal* or *neutral sulphate*, $Zn''SO^4$, also called *white vitriol* or *zinc-vitriol*, is produced by dissolving oxide or carbonate of zinc in dilute sulphuric acid; and on the large scale, by roasting the native sulphide, lixiviating with water, and concentrating the solution by addition of fresh roasted ore. It separates from solution at ordinary temperatures, in right rhombic prisms, containing $Zn''SO^4.7H^2O$, isomorphous with sulphate of magnesium, and exhibiting the combinations $\infty P . P$. (fig. 264, ii. 147), and $P . \bar{P}\infty . \infty P . \infty\breve{P}\infty$; also the hemihedral form $+\frac{P}{2} . -\frac{P}{2} . \infty P . \infty\breve{P}\infty$. (fig. 282, ii. 148). The crystals have a rough metallic taste, and effloresce slightly in dry air. Like the other heptahydrated magnesian sulphates, they give off 6 at. water at about 100°, but the seventh only at a higher temperature (about 260°); indeed it is difficult to obtain the salt perfectly anhydrous without loss of acid. At a bright red heat, the anhydrous salt is completely decomposed, leaving pure oxide of zinc.

The heptahydrated crystals dissolve in about 2⅓ pts. of cold, and in somewhat less than their own weight of boiling water; the solution has an acid reaction. According to Poggiale, 100 pts. of water dissolve at different temperatures the following quantities of zinc-sulphate:—

Temperature. C.	Crystallised $ZnSO^4.7H^2O$.	Anhydrous $ZnSO^4$.
10°	138·21	48·36
20°	161·50	53·10
30°	191·00	58·50
50°	263·80	68·75
100°	653·60	95·60

The salt is insoluble in absolute alcohol. According to Schröder (Ann. Ch. Pharm. cix. 45), a supersaturated solution of zinc-vitriol contained in a glass tube, closed by a plug of cotton-wool, deposits a modification of the heptahydrated salt more soluble than the ordinary salt. The supernatant liquid still remains supersaturated, and, in contact with the air, yields crystals of the ordinary salt, together with crystals of the more soluble modification.

A solution of zinc-sulphate left to crystallise at 30°, yields monoclinic hexhydrated crystals, $Zn''SO^4.6H^2O$, isomorphous with the corresponding magnesium- and nickel-salts. The same hydrate is obtained by heating the ordinary crystals to 52°. A *pentahydrated salt*, $Zn''SO^4.5H^2O$, is obtained, according to Kühn, by boiling the pulverised heptahydrated salt with alcohol of specific gravity 0·856. It also crystallises, according to Pierre and Schindler, from solution between 35° and 50°. A granular *dihydrate*, $Zn'SO^4.2H^2O$, is obtained by boiling the finely pulverised heptahydrate with absolute alcohol; it also separates on adding strong sulphuric acid to a concentrated solution of zinc-sulphate (Kühn). The *monohydrate*, $Zn''SO^4.H^2O$, remains when the heptahydrated salt is dried in the air at 100°, or in a vacuum over oil of vitriol at 20° (Schindler, Graham); it also separates in crystalline grains during the cooling of a boiling saturated solution of zinc-sulphate (Graham). It retains its water at 205°, but gives it up at 238°. (Graham.)

Sulphate of zinc is chiefly used in calico-printing. It also serves as an addition to oils in the manufacture of varnishes; for the preparation of many other zinc-compounds, as of zinc-white; and in medicine for the composition of eye-washes, &c.

Basic Zinc-sulphates.—The *dibasic salt*, $2ZnO.SO^3 = Zn''SO^4.Zn''O$, is produced by digesting a strong solution of zinc-vitriol with oxide or hydrate of zinc as long as anything is dissolved: it does not crystallise (Schindler).—The *tetrabasic salt*, $4Zn''O.SO^3 = Zn''SO^4.3Zn''O$, crystallises from a solution of the preceding by spontaneous evaporation in long flexible needles, containing 10 at. water (Schindler). The same salt is precipitated on adding a small quantity of potash to the solution of the neutral sulphate, as a white bulky powder insoluble in cold water, and separates from a boiling aqueous solution on cooling, in small unctuous crystals, which, according to Kane, contain 2 at. water. It is also formed by heating the neutral sulphate till it is partially decomposed, and boiling the residue with water, or by boiling a solution of the neutral sulphate with zinc-oxide or metallic zinc; in that case also the solution, on cooling, deposits the dihydrated compound $Zn''SO^4.3Zn''O.2H^2O$. (Kühn, Schindler.)

The *hexbasic salt*, $6Zn''O.SO^3.10H^2O = Zn''SO^4.5Zn''O.10H^2O$, is obtained, according to Kane, as a white powder, by treating sulphate of zinc-ammonium with water.—The *octobasic salt*, $8Zn''O.SO^3.2H^2O = Zn''SO^4.7Zn''O.2H^2O$, is precipitated in white bulky flocks on diluting a solution of the dibasic salt with a large quantity of water. The precipitates formed by caustic potash in a solution of zinc-vitriol, are basic salts, varying in composition according to the quantity of alkali used.

All these basic zinc-sulphates, when heated nearly to redness, give off their chemically combined water, without change of appearance; but at a bright red heat, they are decomposed in such a manner that water afterwards extracts from them the neutral salt, leaving zinc-oxide.

Ammoniacal Sulphates of Zinc.—There are several of these compounds, varying in composition according to the quantity of ammonia added to the sulphate of zinc. When ammonia-gas is passed into a hot saturated solution of neutral zinc-sulphate till the precipitate at first formed is redissolved, *sulphate of zinc-ammonium*, $Zn''SO^4.2NH^3.H^2O = (N^2H^6Zn)''SO^4.H^2O$, separates on cooling in fine semi-crystalline starch-like granules. The water may be expelled by prolonged fusion. If the ammoniacal solution just mentioned be left to evaporate at ordinary temperatures, it yields crystals of the compound $Zn''SO^4.4NH^3.4H^2O$ or $[N^2.H^4(NH^4)^2Zn]''SO^4.4H^2O$, which give off 2 at. water in drying, and quickly effloresce. Above 27° they give off another atom of water, leaving the compound $Zn''SO^4.4NH^3.H^2O$; and this when carefully melted yields a gummy mass of zincammonium-sulphate, $Zn''SO^4.2NH^3.H^2O$, and ultimately the same compound in the anhydrous state (Kane). The compound, $Zn''SO^4.5NH^3$, is produced by the action of dry ammonia-gas on zinc sulphate, and forms a white powder which is dissolved by water with partial separation of zinc-oxide (H. Rose).—When zinc-sulphate supersaturated while hot with ammonia, is boiled till the odour of free ammonia is no longer perceptible, a precipitate is formed, consisting of $(4ZnO.SO^3).4NH^3.4H^2O$. (Schindler.)

Double Salts.—*Ammonio-zincic sulphate*, $Zn(\overset{''}{N}H^4)^2(SO^4)^2.6H^2O$, and the corresponding *potassium-salt*, are isomorphous with the corresponding magnesium-salts.

Sodio-zincic sulphate, $Zn''Na^2(SO^4)^2.4H^2O$, is produced, according to Graham, by mixing the concentrated solutions of zinc-sulphate and acid sodic sulphate, and evaporating to the crystallising point. It is very deliquescent.

Magnesio-zincic sulphate, $Zn''Mg''(SO^4)^2.14H^2O$, crystallises, according to Pierre, at ordinary temperatures, in fine rhombic prisms; it retains 2 at. water at 200°. The salt crystallised above 35° contains only 10 at. water.

Zinco-aluminic sulphate or *zinc-alum* is analogous in composition to common alum. (Kane.)

Sulphates of Zirconium.—The *neutral* or *normal sulphate*, $Zr^{iv}(SO^4)^2 = Zr^{iv}O^2.2SO^3$, is obtained by dissolving oxide or hydrate of zirconium, free from potash, in an excess of sulphuric acid; evaporating the solution to dryness; and heating the residue for a quarter of an hour to a temperature just below redness. The salt loses the whole of its acid at a full red heat. A neutral solution of the salt yields on evaporation, a gummy mass, which, when further dried, becomes white and full of fissures. If, however, the solution contains free acid, hydrated crystals are obtained, which may be freed from adhering acid by means of alcohol. The crystals fuse when heated, giving off their water, and swelling up like alum.

The anhydrous salt dissolves very slowly but completely in cold, and rapidly in hot water. Ammonia added in excess to the solution, precipitates pure zirconia free from sulphuric acid. Alcohol throws down a mixture of the normal and tribasic sulphates, which, after being washed for a considerable time with alcohol, is entirely converted into the tribasic sulphate. (Berzelius.)

The *dibasic sulphate*, $Zr^{iv}O^2.SO^3 = Zr^{iv}(SO^4)^2.Zn^{iv}O^2$, is formed by, saturating a concentrated solution of the normal salt with hydrate of zirconium. On evaporating the liquid, a mass of salt is obtained which is gummy and fissured at first, but when further dried becomes white and opaque. The salt, when heated, swells up like alum, and parts with its water, but a white heat is required to expel the acid. It dissolves in a very small quantity of water. By a larger addition of water, the solution is resolved into the tribasic salt, which is precipitated, and the normal salt, which remains in solution. (Berzelius.)

The *tribasic sulphate*, $3ZrO^2.2SO^3 = Zr(SO^4)^2.2ZrO^2$, is obtained by precipitating the normal salt with alcohol, and washing the precipitate first with alcohol and then with water; or by diluting a solution of the dibasic salt with a large quantity of water. It forms white flakes, insoluble in water, but soluble in hydrochloric acid. (Berzelius.)

A *hexbasic salt*, $3ZrO^2.SO^3 = Zn(SO^4)^2.5ZnO^3$, is produced by saturating a solution of a zirconium-salt at the boiling heat with sulphate of potassium, or by mixing the zirconium-solution with a hot saturated solution of sulphate of potassium. It separates as a white precipitate, and by saturating the supernatant liquid with carbonate of potassium, the whole of the zirconium may be brought into the precipitate (Berzelius, Hermann). According to Berzelius, the precipitate always contains small quantities of potash, probably chemically combined, inasmuch as it is produced only by sulphate of potassium, and not by sulphate of sodium. It is insoluble in a solution of potassic sulphate, but dissolves partially in pure water, and the water with which it is washed becomes turbid (Berzelius). Sulphate of ammonium reacts with zirconium-salts in the same manner as sulphate of potassium. (Berzelius.)

Zirconia fused with acid sulphate of potassium forms a double salt, which, in the fused state, is perfectly transparent. Water dissolves only the potassium-salt, leaving the sparingly soluble zirconium-salt just mentioned (Berzelius). Warren (Pogg. Ann. cii. 449; Jahresb. 1857, p. 158), by precipitating a solution of neutral zirconic sulphate with neutral and acid sulphate of potassium, has obtained some double salts of complicated and very doubtful composition.

ALCOHOLIC SULPHATES. SULPHURIC ETHERS.

Alcohols treated with strong sulphuric acid, yield acid sulphuric ethers represented by the general formula, $\frac{R}{H}SO^4$:

$$\left.\begin{matrix}R\\H\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}SO^4 = H^2O + \left.\begin{matrix}R\\H\end{matrix}\right\}SO^4.$$

Alcohol. Sulphuric acid. Acid ether.

There are also a few neutral sulphuric ethers represented by the formula $\left.\begin{matrix}R\\R\end{matrix}\right\}SO^4$; they are formed, not by the action of sulphuric acid upon alcohols, but of sulphuric anhydride upon neutral ethers (alcoholic oxides).

Allyl-sulphuric Acid, $C^3H^6SO^4 = \left.\begin{matrix}C^3H^4S^2\\H\end{matrix}\right\}SO^4 = \left.\begin{matrix}(SO^2)''\\C^3H^5\\H\end{matrix}\right\}O^2$. (Cahours and Hofmann, Chem. Soc. Qu. J. x. 316).—When allylic alcohol is added by drops to about an equal volume of strong sulphuric acid, the mixture becomes heated without blackening: and in adding seven or eight times the volume of water, and neutralising with carbonate of barium, the liquid yields, by evaporation, white shining crystals of baric allyl-sulphate $(C^3H^5)^2Ba''(SO^4)^2$.

Amylsulphuric acid, $(C^5H^{11})HSO^4$. *Sulphamylic acid.* (Cahours, Ann. Ch. Phys. [2], lxx. 86.—Kekulé, Ann. Ch. Pharm. lxxv. 275.)—A mixture of equal parts of amylic alcohol and oil of vitriol, after standing for some time, till water no longer separates amylic alcohol from it, is diluted with water; the resulting crude amyl-sulphuric acid is saturated with carbonate of barium; the solution filtered from the sulphate of barium is evaporated; and the crystals of amylsulphate of barium obtained after cooling are freed from the mother-liquor upon filter-paper; and purified by shaking up their aqueous solution with animal charcoal, and twice crystallising by spontaneous evaporation. The solution of these crystals, precipitated by the proper quantity of sulphuric acid, then filtered and evaporated, yields the pure acid. (Cahours). Kekulé prefers preparing the lead-salt and decomposing it with sulphuretted hydrogen, after which he carefully evaporates the colourless filtrate to a thin syrup.

Amyl-sulphuric acid is a colourless, thin syrup which sometimes deposits slender needles by spontaneous evaporation. (Kekulé did not obtain any crystals.) It tastes acid and bitter (sharply acid, according to Kekulé), and reddens litmus strongly. (Cahours.) It dissolves readily in water and in alcohol.

The concentrated aqueous acid decomposes spontaneously into amyl-alcohol and sulphuric acid, slowly in the cold and in a vacuum or when exposed to the air; quickly on boiling; the more quickly as it is more concentrated. It is decomposed by chlorine in the cold, and by nitric acid when heated.

The amylsulphates or sulphamylates $(C^5H^{11})MSO^4$, and $(C^5H^{11})^2M''(SO^4)^2$, are generally crystallisable, have a bitter taste and are soapy to the touch. The crystals generally contain water, and in that case are often efflorescent. When their aqueous solution is boiled, they are resolved into sulphate, free sulphuric acid and amylic alcohol. This decomposition takes place slowly at ordinary temperatures, even in the crystallised salts; nevertheless, these crystallised salts may generally be dehydrated at 100° before decomposition begins. All amylsulphates dissolve in water and in alcohol, very sparingly in ether. Most of them in the crystalline state or in aqueous solution are decomposed by prolonged contact with the air, giving off amylic alcohol and leaving a metallic sulphate; the decomposition is accelerated by heat. By dry distillation they leave metallic sulphate mixed with charcoal, and give off a combustible gas together with carbonic and sulphurous anhydrides, and an oil containing amylene, other hydrocarbons polymeric therewith, amylic ether $(C^5H^{11})^2O$, and probably also amylic sulphate $(C^5H^{11})^2SO^4$; at all events, the distilled product contains sulphur.

Amylsulphate of Aluminium forms a gelatinous mass, soluble in water, alcohol, and ether, very deliquescent, and easily decomposible.

Amylsulphate of Ammonium.—The filtrate obtained by precipitating the calcium-salt with carbonate of ammonia, yields by spontaneous evaporation, colourless, bitter crystalline scales, and by evaporation over the water-bath a nodular crystalline mass. The crystals give off nothing at 100°, begin to decompose at 140°, and burn away, leaving a residue of charcoal. They deliquesce slightly in damp air, and dissolve very readily in water, on which they move briskly about; they are less soluble in alcohol, and insoluble in ether.

The *barium-salt* $(C^5H^{11})^2Ba''(SO^4)^2.2H^2O$, prepared as above, crystallises by spontaneous evaporation, in large very flexible rhombic tables. The crystals effloresce in dry air and give off 6·66 per cent, (1 at.) water *in vacuo*. They begin to decompose at 95°, melting at the same time, if they have not been previously dried. They give off an oil somewhat above 200°, and leave sulphate of barium mixed with charcoal. Their aqueous solution is resolved by longer boiling, into amylic alcohol, sulphuric acid, and sulphate of barium. They dissolve very readily in water, more readily in warm than in cold alcohol, but are insoluble in ether.

The *calcium-salt*, $(C^5H^{11})^2Ca''(SO^4)^2.2H^2O$, obtained by saturating amyl-sulphuric acid with chalk, forms mammellated crystals, soft to the touch, very soluble in water, especially in hot water, soluble in alcohol, insoluble in ether. It has a bitter and pungent taste. An aqueous solution, saturated and limpid at ordinary temperatures, becomes turbid at the boiling heat. The crystals effloresce in dry air, give off the whole of their water (8·55 per cent.) in a vacuum, and are gradually decomposed by contact with the air. The salt, heated to 250° in a sealed tube with alcoholic ammonia, yields sulphate of calcium and sulphate of amylamine. (Berthelot, Compt. rend. xxxvi. 1098.)

The *cobalt-salt* is obtained, by precipitating the barium-salt with sulphate of cobalt, and evaporating the filtrate, in rose-coloured laminæ, very soluble in water.

Cupric salt, $(C^5H^{11})^2Cu''(SO^4)^2.2H^2O$.—The blue solution of carbonate of copper in the acid yields, when left over oil of vitriol, large elongated tables which are permanent in the air, dissolve readily in water and weak alcohol, less readily in absolute alcohol, and are insoluble in ether.

The *ferric salt*, obtained by dissolving ferric hydrate in the aqueous acid, forms small, yellow, easily decomposible, deliquescent, crystalline granules.—The *ferrous salt* is produced by dissolving metallic iron in the aqueous acid. The pale green, sweetish-bitter solution reddens litmus, and when evaporated, deposits brown flakes of ferric oxide, together with pale green crystalline grains of the ferrous salt. These crystals quickly turn yellow on exposure to the air, dissolve in water and alcohol, and with green colour in ether.

The *lead-salt*, $(C^5H^{11})^2Pb''(SO^4)^2.H^2O$, obtained by saturating the acid with carbonate of lead, forms mammellated groups of small laminæ, very soluble in water, acid to test-paper, soluble in alcohol, insoluble in ether, and having a bitter-sweet taste. The solution decomposes slowly in contact with the air, rapidly at the boiling heat.

The *magnesium-salt*, $(C^5H^{11})^2Mg''(SO^4)^2.4H^2O$, is obtained by spontaneous evaporation in elongated rhomboïdal laminæ, which, have a fine nacreous lustre, and are with difficulty deprived of the whole of their water of crystallisation.

The *manganese-salt*, $(C^5H^{11})^2Mn''(SO^4)^2.4H^2O$, forms nearly colourless crystals, permanent in the air; the solution, however, gradually decomposes.

Mercuric salt.—The yellow solution of mercuric oxide in amylsulphuric acid yields, by evaporation in a vacuum, dark yellow crystalline nodules, soapy and glutinous to the touch, having an extremely sharp and bitter taste; they contain 2 at. water, decompose after keeping for some time, and deliquesce in damp air.

The *nickel-salt*, $(C^5H^{11})^2Ni''(SO^4)^2.2H^2O$, crystallises by evaporation in a vacuum, in nodules of green, elongated laminæ, which deliquesce in moist air.

The *potassium-salt*, $(C^5H^{11})KSO^4$, separates from its solution by spontaneous evaporation in colourless tufts of needles, having a very bitter taste, or in nodules composed of needles having a silky lustre. These crystals effloresce on exposure to the air, and turn slightly brown, giving off amylic alcohol and sulphuric acid. In a vacuum or at 100°, they give off 3·99 per cent. (1 at.) of water, without further decomposition, swell up strongly at 170°, then melt, and leave a black scum. The salt dissolves readily in water and in weak alcohol, less readily in strong alcohol, from the hot solution in which it crystallises in slender needles, and is insoluble in ether.

Silver-salt, $(C^5H^{11})AgSO^4$.—The solution of carbonate of silver in the slightly heated acid yields, by evaporation, colourless laminæ, which dissolve very easily in water, blacken on exposure to the air, and dissolve in alcohol but not in ether.

The *sodium-salt*, $(C^5H^{11})NaSO^4$, is obtained by precipitating the calcium-salt with carbonate of sodium, and spontaneous evaporation of the filtrate, in nodules set with small crystals. These swell up at 35° [135?] softening, and giving off water, and begin to undergo further decomposition at 145°. They dissolve abundantly in cold water, and in all proportions in hot water; from hot alcohol they crystallise in long radiated laminæ; they do not dissolve in ether.

The *strontium-salt*, $(C^5H^{11})^2Sr''(SO^4)^2.2H^2O$, forms white crystallised nodules, which turn brown in the air, leave 39·82 per cent. sulphate of strontium when ignited, dissolve readily in water and weak alcohol, with difficulty in absolute alcohol, and not at all in ether.

The *zinc-salt*, $(C^5H^{11})^2Zn''(SO^4)^2.2H^2O$, forms nacreous scales grouped in nodules, soluble in water and in alcohol, and decomposing at 110°.

Butyl-sulphuric acid. See TETRYL-SULPHURIC ACID.

Capryl-sulphuric acid. See OCTYL-SULPHURIC ACID.

Cetyl-sulphuric acid. $(C^{16}H^{33})HSO^4$.—*Sulphocetic acid*: (Dumas and Péligot, Ann. Ch. Phys. [2] lxii. 4.—Köhler, Jahresb. 1856, p. 579.—Heintz, Pogg. Ann. cii. 257; Jahresb. 1857, p. 445.)—The potassium-salt of this acid is produced by mixing ethal with strong sulphuric acid, at the temperature of the water-bath; dissolving the mass in alcohol; saturating with alcoholic potash; separating the liquid from the deposited sulphate of potassium; concentrating it; digesting the cetyl-sulphate of potassium, which separates with alcohol, to free it from excess of ethal; and purifying it by repeated crystallisation from boiling alcohol.

Cetyl-sulphate of potassium, $(C^{16}H^{33})KSO^4$, crystallises in soft nacreous laminæ, composed of interlaced needles; it is moderately soluble in hot alcohol, less soluble in boiling water, insoluble in ether, not fusible. Heated with cyanide of potassium, it yields cyanide of cetyl (i. 840).

Ethyl-sulphuric acid. $(C^2H^5)HSO^4$. *Sulphethylic acid. Sulphovinic acid.* (Dabit, Ann. Chem. xxxiv. 300; xliii. 101.—Sertürner, Gilb. Ann. lx. 53; lxiv. 6, 7.—A. Vogel, *ibid.* lxiii. 81.—Gay-Lussac, Ann. Ch. Phys. [2], xiii. 76.—Hennell, Phil. Trans. 1826, p. 240; 1828, p. 365.—Dumas and Boullay, Ann. Ch. Phys. xxxvi. 300.—Serullas, *ibid.* xxxix. 153.—Liebig and Wöhler, Ann. Ch. Pharm. i. 37.—Liebig, *ibid.* xiii. 27.—Magnus, *ibid.* vi. 52.—Marchand, Pogg. Ann. xxviii. 454; xxxii. 345; xli. 595.—Müller, Ann. Ch. Phys. [3], xix. 22.—Berthelot, Compt. rend. xxxvi. 1098.—Gm. viii. 415; x. 511).—This acid, produced by the action of strong sulphuric acid upon alcohol, ether, or ethylene, was first noticed by Dabit (in 1800), in the residues of the preparation of ether by heating alcohol with sulphuric acid; afterwards (1819) by Sertürner. Hennel, in 1826, announced that he had produced it by the direct combination of ethylene (olefiant gas) with sulphuric acid; but this result was for a long time doubted, the formation of the ethyl-sulphuric acid being attributed to the presence of alcohol or ether vapour in the olefiant gas. The more recent experiments of Berthelot, however, have confirmed Hennel's statement, and shown that ethyl-sulphuric acid may be formed by briskly agitating strong sulphuric acid with perfectly pure ethylene gas, obtained either from alcohol, or from coal-gas (by absorbing it with iodine, and decomposing the ethylenic iodide with potash), or produced by the direct combination of hydrogen with acetylene, (i. 112), or in various other ways from inorganic materials (ii. 565.)—On the formation of ethyl-sulphuric acid from alcohol, see Alcohol (i. 76).

Preparation.—A mixture of equal parts of strong sulphuric acid and strong alcohol is heated to about 100°, and after standing in a warm place for 24 hours, diluted with water, and saturated with carbonate of barium or carbonate of lead; the solution is then filtered from the precipitated sulphate of barium or lead; and the filtrate carefully evaporated to the crystallising point. The crystals of baric or plumbic ethylsulphate are then redissolved in water; the solution is decomposed with an exactly equivalent quantity of sulphuric acid—or better, in the case of the lead-salt, with sulphydric acid;—and the filtrate is concentrated in a vacuum over oil of vitriol or chloride of calcium.

Properties.—Ethyl-sulphuric acid, concentrated to the highest degree that it will bear without decomposition, is a limpid, oily, very sour liquid, of specific gravity 1·315 to 1·317 at 16°. It dissolves in all proportions in water and in alcohol, but is insoluble in ether.

The dilute acid decomposes gradually at ordinary temperatures, quickly on boiling, into alcohol and sulphuric acid. The concentrated acid is resolved at a moderate degree of heat into ether and sulphuric acid, but at a higher temperature it suffers more complete decomposition, giving off ethylene gas and sulphurous oxide, and leaving a carbonaceous residue. Heated with alcohol to 130°—140°, it yields ether and sulphuric acid, (i. 76):

$$(C^2H^5)HSO^4 + (C^2H^5)HO = (C^2H^5)^2O + H^2SO^4.$$

Heated with manganic peroxide or potassic chromate, it yields aldehyde. (Jacquemin and Liès.-Bodard, Jahresb. 1857, p. 345.)

Ethyl-sulphates or sulphovinates, $(C^2H^5)MSO^4$ and $(C^2H^5)^2M''(SO^4)^2$. Ethylsulphuric acid is a strong acid, which decomposes carbonates and sulphites, and neutralises bases completely. Some of the ethyl-sulphates are anhydrous; others contain water of crystallisation, which for the most part they give off in a vacuum over oil of vitriol. They are likewise dehydrated by heating to 100°, or in some cases to higher temperatures, with partial decomposition. They all dissolve easily in water, some also in alcohol, and a few, the ammonium-salt, for example, in ether. Most ethylsulphates are permanent in the air, but the ammonium-, lithium-, sodium-, and zinc-salts are very deliquescent. When dissolved in a small quantity of water, they produce a perceptible degree of cold.

The ethyl-sulphates may be prepared by saturating the acid with oxides or carbonates, or by decomposing the barium- or lead-salt with the corresponding sulphates;

the ethyl-sulphates of the alkali-metals, also by decomposing the barium- or lead-salt with an alkaline carbonate.

The ethyl-sulphates in aqueous solution are decomposed by ebullition, but the decomposition is completely prevented by adding a few drops of caustic potash. Some of them, especially the strontic, baric, plumbic, ferric, manganous, argentic, aluminic, and uranic salts, undergo spontaneous decomposition, while others may be kept for years without alteration. They are decomposed by dry distillation, first giving off ether and alcohol, together with their water of crystallisation, afterwards heavy oil of wine (probably a mixture of neutral ethylicsulphate and oily hydrocarbons), together with carbonic and sulphurous anhydrides, and olefiant gas, and leaving metallic sulphate mixed with charcoal. Heated in contact with the air, they burn with a faint bluish flame. Heated with strong *sulphuric acid*, they give off ether, and, with the dilute acid, alcohol. Heated with *hydrate of potassium*, they yield alcohol, and with *quicklime* they give off, first alcohol, afterwards heavy oil of wine and olefiant gas.—Heated with *mangaric peroxide* or *potassic chromate*, they yield aldehyde, together with wine-oil and other products of decomposition. (**Jacquemin** and **Liés-Bodard.**)

The ethyl-sulphates distilled with other salts yield compound ethers; for example:

$$\underset{\substack{\text{Potassic}\\\text{acetate.}}}{C^2H^3KO^2} + \underset{\substack{\text{Potassic}\\\text{Ethyl-sulphate.}}}{C^2H^5KSO^4} = K^2SO^4 + \underset{\substack{\text{Ethylic}\\\text{acetate.}}}{C^2H^3(C^2H^5)O^2}.$$

Compound ethers are often prepared by this method. According to **Nadler** (Ann. Ch. Pharm. cxvi. 173; Jahresb. 1860, p. 403), ethyl-sulphate of potassium distilled with *nitrate of potassium*, yields, not ethylic nitrate, but a heavy oily liquid consisting of aceto-ethyl-nitrate, $C^6H^{14}N^2O^7$, a compound of 2 at. ethylic-nitrate and 1 at. aldehyde ($2C^2H^5NO^3 + C^2H^4O$), the latter being produced from ethylic nitrate by elimination of NO^2H.

When a cold concentrated aqueous solution of an ethyl-sulphate is electrolysed with platinum-plates for electrodes, the inorganic base is separated at the negative pole, with evolution of hydrogen, whilst free sulphuric acid is eliminated at the positive pole, together with oxygen and carbonic dioxide, an odour of aldehyde being also perceptible. If the positive pole is formed of amalgamated zinc, it becomes coated with a film of ethyl-sulphate of zinc, but neither aldehyde nor sulphuric acid makes its appearance. (**Guthrie**, Ann. Ch. Pharm. xcix. 64.)

Ethyl-sulphate of Aluminium is gummy and deliquescent.

The *ammonium-salt*, $(C^2H^5)(NH^4)SO^4$, forms anhydrous crystals which melt at 62°, are very deliquescent, and very soluble in water, alcohol, and ether.

The *barium-salt*, $(C^2H^5)^2Ba''(SO^4)^2.2H^2O$, crystallises in monoclinic prisms, isomorphous with the methyl-sulphate, and exhibiting the combination ∞P . ∞P∞ . oP . −P∞ . +P. Axes, $a : b : c = 0{\cdot}8229 : 0{\cdot}9790 : 1$. Angle $b : c = 84° 39'$; ∞P : ∞P (orthod.) = 80° 20′; +P : +P = 96° 44′; oP : ∞P = 93° 26′; ∞P∞ : −P∞ = 121° 18′. Cleavage perfect, parallel to ∞P∞ (**Schabus**, *Bestimmung der Krystallgestalten, &c.*). The crystals contain 8·48 per cent. water of crystallisation, which they give off in a vacuum. The anhydrous salt does not alter at 100°, but the hydrated salt undergoes slight decomposition at that temperature. The hydrated salt dissolves in 0·92 pts. water at 17°; it is soluble also in alcohol of ordinary strength. Its aqueous solution, when boiled, becomes turbid and acid, and deposits sulphate of barium, and the filtered liquid, saturated with carbonate of barium, yields parathionate of barium, isomeric with the ethyl-sulphate (iv. 354).

The *cadmium-salt*, $(C^2H^5)^2Cd''(SO^4)^2.2H^2O$, forms long limpid prisms, very soluble in water and in alcohol, insoluble in ether, and giving off their water of crystallisation in a vacuum.

The *calcium-salt* $(C^2H^5)^2Ca''(SO^4)^2.2H^2O$, forms monoclinic crystals, apparently isomorphous with the barium-salt. Dominant faces ∞P, ∞P∞. Angle ∞P : ∞P (orthod.) = 80° 8′ (**Schabus**). The crystals are permanent in the air, and contain 11·7 per cent. water, which they give off in a vacuum, or when heated to 80°. One part of the salt dissolves in 1 pt. water at 8°, in 0·8 pt. at 17°, in 0·63 pt. at 30°, and in all proportions in boiling water. The salt is less soluble in alcohol, insoluble in ether. The anhydrous salt begins to decompose at about 120°.

The *cobalt-salt*, $(C^2H^5)^2Co''(SO^4)^2.2H^2O$, forms dark-red crystals, permanent in the air, very soluble in water and in alcohol, insoluble in ether.

The *cupric salt*, $(C^2H^5)^2Cu''(SO^4)^2.4H^2O$, crystallises in right rectangular prisms, or laminæ of a fine blue colour, very soluble in water and in alcohol, insoluble in ether.

The *ferric salt*, obtained by dissolving ferric hydrate in ethylsulphuric acid, crystallises with difficulty in yellow deliquescent tables, soluble in water and in alcohol, insoluble in ether.

The *ferrous salt*, obtained by dissolving metallic iron in the acid, crystallises in greenish prisms, which alter very quickly.

Lead-salts.—The *normal salt*, $(C^2H^5)Pb''(SO^4)^2.2H^2O$, crystallises in colourless transparent tables, very soluble in water and in alcohol, and having an acid reaction. They contain 7·28 per cent. water of crystallisation, which they give off in a vacuum, or when heated. They undergo gradual decomposition. The solution of this salt, digested with recently precipitated oxide of lead, yields an uncrystallisable basic salt, $(C^2H^5)^2Pb''S^2O^8.Pb''O$, soluble in water and in alcohol. By supersaturating the solution of the neutral salt with ammonia, evaporating, redissolving the residue in water, and again evaporating, scales are obtained containing lead and ammonia.

The *lithium-salt*, $C^2H^5LiSO^4.H^2O$, forms deliquescent crystals.

The *magnesium-salt*, $(C^2H^5)^2Mg''(SO^4)^2.4H^2O$, forms crystals very soluble in water, insoluble in alcohol and in ether, and containing 20·8 per cent. water of crystallisation, half of which goes off at 80°, the rest at 90°.

The *manganese-salt*, $(C^2H^5)^2Mn''(SO^4)^2.4H^2O$, forms roseate tables, permanent in the air, very soluble in water and in alcohol, insoluble in ether.

The *mercuric salt* is very unstable and deliquescent.

The *nickel-salt*, $(C^2H^5)^2Ni''(SO^4)^2.2H^2O$, forms green, very soluble, granular crystals.

The *potassium-salt*, $C^2H^5KSO^4$, crystallises easily in large, colourless, anhydrous tables or laminæ belonging to the monoclinic system, and exhibiting the combination $\infty P . oP . [P\infty]$. Axes $a : b : c = 0·5730 : 0·6149 : 1$. Angle $b : c = 80° 27$. $\infty P : \infty P$ (othod.) $= 86° 53'$; $[P\infty] : [P\infty] = 60° 30'$; $oP : \infty P = 96° 33'$. Cleavage perfect parallel to oP (Schabus). It has a sweetish saline taste, dissolves in 0·8 pts. water at 17°, deliquesces in moist air, is insoluble in absolute alcohol and in ether.

The *silver-salt*, $C^2H^5AgSO^4.H^2O$, forms shining scales, which dissolve in water and in alcohol, and do not give off their water of crystallisation till raised to a temperature at which they decompose.

The *sodium-salt*, $C^2H^5NaSO^4.H^2O$, crystallises in hexagonal plates, which contain 10·78 per cent. water of crystallisation, effloresce in warm air, and melt to a colourless liquid at 86°. The anhydrous salt does not melt or decompose till heated above 100°. It dissolves in 0·61 pts. water at 17°, and is even more deliquescent than the potassium-salt.

The *strontium-salt*, $(C^2H^5)^2Sr''(SO^4)^2$, forms anhydrous crystals very soluble in water.

The *uranic salt* is yellow, and decomposes between 60° and 70°.—The *uranous salt* crystallises with difficulty and is deliquescent.

The *zinc-salt*, $(C^2H^5)^2Zn''(SO^4)^2.2H^2O$, forms large colourless tables, very soluble in water and in alcohol, insoluble in ether.

DIETHYLIC OR NEUTRAL ETHYLIC SULPHATE, OR ETHYLIC ETHYLSULPHATE, $(C^2H^5)^2SO^4 = (C^2H^5)^2O.SO^3$. *Sulphuric ether.* (Wetherill, Ann. Ch. Pharm. lxvi. 117.)—This compound is produced by direct combination of ethylic oxide with sulphuric anhydride; also by the action of sulphuric anhydride on absolute alcohol, the alcohol being first dehydrated, and the ether thus produced uniting with another portion of sulphuric anhydride.

Preparation.—Vapour of sulphuric anhydride is passed into a flask containing ether and surrounded by a freezing mixture. The vapour, by its great density, sinks to the bottom of the flask and comes in contact with the ether, and the liquid after a while acquires a syrupy consistency, so that it requires to be shaken up with an equal bulk of ether and four times its bulk of water. It then separates into two layers, the upper of which, containing the ethylic sulphate, must be separated from the lower, which is strongly acid, and contains sulphuric, sulphurous, ethionic, and ethyl-sulphuric acids (p. 625), mixed, if the temperature has not been kept low enough, with black carbonaceous particles, and also with isethionic and methionic acids, resulting from the decomposition of the ethionic acid. The ethereal liquid is then shaken up with milk of lime to remove the sulphurous acid—whereby part of the colouring matter is at the same time removed—then washed with water, filtered, and the ether distilled off. In the retort there remains an oily liquid, containing a trace of ether, and having a slightly acid reaction, arising from the decomposition of part of the ethylic sulphate, which takes place, when the liquid is heated, by the action of the water taken up by the ether. The oil is then transferred from the retort into a basin, and washed with a small quantity of water, the last portions of which are carefully removed by strips of bibulous paper, after which the liquid is dried in a vacuum over sulphuric acid.

Properties.—Ethylic sulphate is an oily liquid, colourless when pure, but generally exhibiting a yellow tint. It has a sharp taste, and smells like oil of peppermint. Specific gravity 1·120. It makes greasy spots on paper, which however disappear after a while.

1. *Decompositions.*—This compound is very easily decomposed when heated in contact with the air, so that it can only be distilled in an atmosphere of carbonic

anhydride. At 100°, vapours begin to rise, which condense in small oily drops; between 110° and 120°, the oil passes over unchanged; but between 130° and 140°, the liquid blackens, gives off sulphurous anhydride and alcohol, and at a higher temperature, the same products mixed with olefiant gas.—2. Ethylic sulphate heated with *water*, forms, without separation of wine-oil, a very acid liquid, which gives off alcohol when boiled; and when treated with carbonate of barium, yields three soluble barium-salts—viz., methionate, ethylsulphate, and isethionate of barium. The first of these salts is, however, so small in quantity, that it can only be regarded as a secondary product. The formation of the other products may be represented by the following equation:

$$\underset{\substack{\text{Ethylic}\\\text{sulphate.}}}{3(C^2H^5)^2SO^4} + 3H^2O = \underset{\substack{\text{Ethylsulphuric}\\\text{acid.}}}{2(C^2H^5)HSO^4} + \underset{\substack{\text{Isethionic}\\\text{acid.}}}{(C^2H^4)H^2SO^4} + \underset{\text{Alcohol.}}{3(C^2H^5.H.O)}$$

3. Ethylic sulphate is decomposed by an excess of *sulphuric anhydride*, yielding ethylsulphuric acid, ethionic acid, and ethionic anhydride; hence the formation of these products in the preparation of the compound:

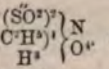
$$\underset{\substack{\text{Ethylic}\\\text{sulphate.}}}{2C^4H^{10}SO^4} + 5SO^3 = \underset{\substack{\text{Ethylsul-}\\\text{phuric acid.}}}{C^2H^6SO^4} + \underset{\substack{\text{Ethionic}\\\text{acid.}}}{C^2H^6S^2O^7} + \underset{\substack{\text{Ethionic}\\\text{anhydride.}}}{2C^2H^4S^2O^6}.$$

4. *Sulphydric acid* does not act on ethylic sulphate at ordinary temperatures, but *sulphydrate of potassium* decomposes it, forming mercaptan and sulphate of potassium:

$$(C^2H^5)^2SO^4 + 2KHS = 2(C^2H^5)HS + K^2SO^4.$$

5. *Chlorine* does not decompose ethylic sulphate at ordinary temperatures, but combines with it, forming a green liquid, which, on addition of water, yields the compound in its original state.—6. *Potassium* does not act on sulphuric ether at ordinary temperatures, but on the application of heat, decomposes it, with evolution of light and heat, forming mercaptan, together with other products.—7. Sulphuric ether dissolves in fuming *nitric acid*, and is precipitated from the solution by water. On adding caustic potash till the liquid is nearly neutral, and applying heat, *nitrous ether*, $C^2H^5NO^2$, is evolved.

SULPHETHAMIC ACID, $C^8H^{23}NS^2O^8 = 2C^4H^{10}SO^4.NH^3 =$



$$\left.\begin{matrix}(\overset{\prime\prime}{SO^2})^2\\(C^2H^5)^4\\H^3\end{matrix}\right\}\begin{matrix}N\\O^4\end{matrix}$$

(Strecker, Ann. Ch. Pharm. lxxv. 46.)—Ethylic sulphate absorbs ammonia-gas with rise of temperature; the product dissolves easily in water or in alcohol, and the solution yields, by evaporation, groups of crystalline laminæ, consisting of sulphethamate of ammonium. This salt, treated with oxide of lead, yields the sulphethamate of that base, which, when decomposed by sulphuretted hydrogen, yields the free acid. The solution of sulphethamic acid may be concentrated by evaporation; but at the boiling heat it decomposes, yielding free sulphuric acid.

Sulphethamate of Ammonium, $C^8H^{22}(NH^4)NS^2O^8$, deliquesces in moist air, melts below 100°, and burns at a stronger heat, with a faintly luminous flame, emitting an odour like that of ethylic sulphide. It dissolves easily in water and in alcohol, not in ether. The solution is neutral, and does not precipitate metallic salts. It is decomposed by alkalis in the cold, with evolution of ammonia. When mixed with chloride of barium and nitric acid, it does not yield an immediate precipitate of sulphate of barium, but the mixture becomes cloudy after long boiling.

When moist sulphethamate of ammonium is heated to 100°, or a little above, it quickly becomes acid, and its solution is then precipitated by barium-salts. If the ammonia be precipitated from a solution of the salt by platinic chloride and hydrochloric acid, and the liquid containing the excess of platinic chloride evaporated over the water-bath, crystals of chloroplatinate of ethylamine are obtained. It appears then that sulphethamic acid is decomposed by heat, under the influence of acids, into ethylamine and sulphuric acid, other products not yet examined being likewise produced. Possibly alcohol and isethionic acid are formed at the same time, according to the equation:

$$C^8H^{23}NS^2O^8 + 2H^2O = C^2H^7N + C^2H^6SO^4 + 2C^2H^6O + H^2SO^4.$$

A solution of the ammonium-salt evaporated over the water-bath with baryta, leaves nothing but sulphate of barium. On boiling it with carbonate of barium or oxide of lead, till all the ammonia is expelled, and then distilling with potash, ethylamine is obtained.

Sulphethamate of Barium is obtained by boiling the aqueous ammonium-salt for a short time with carbonate of barium, and remains on evaporation as a very soluble mass, crystallising with difficulty.—The *lead-salt*, prepared in like manner with oxide of lead, the excess of lead being removed by carbonic acid, crystallises in needles, very soluble in water and alcohol of ordinary strength, slightly soluble in absolute alcohol. (Strecker.)

Methylsulphuric Acid, $(CH^3)HSO^4$. *Sulphomethylic Acid.* (Dumas and Péligot, Ann. Ch. Phys. lviii. 54; lxi. 199.—Kane, Phil. Mag. vii. 397.)—Produced in large quantity by mixing 1 pt. of wood-spirit with 2 pts. of strong sulphuric acid, the mass becoming hot, and sometimes crystallising by spontaneous evaporation. It is obtained pure by completely decomposing a solution of its barium-salt with sulphuric acid; also (according to Liebig) by dissolving neutral methylic sulphate in boiling water, and leaving the solution to evaporate. It forms colourless needles, soluble in water and in alcohol, and very unstable.

The methylsulphates, CH^3MSO^4, are all very soluble in water. Those of the alkali-metals yield, by distillation, a large quantity of methylic sulphate, with a residue of alkaline sulphate:

$$2CH^3KSO^4 = (CH^3)^2SO^4 + K^2SO^4.$$

When distilled with other salts, they yield methylic ethers by double decomposition, just like the ethylsulphates.

The *barium-salt*, $(CH^3)^2Ba''(SO^4)^2.2H^2O$, obtained by saturating a mixture of sulphuric acid and wood-spirit with carbonate of barium, is deposited, by evaporation in a vacuum, in beautiful nacreous tables or laminæ, very soluble in water. The crystals are monoclinic, exhibiting the combination ∞P . ∞P∞ . [∞P∞] . oP . [P∞]. Axes, $a : b : c = 0·824 : 1·907 : 1$. Angle $b : c = 83° 30'$; ∞P : ∞P (clinod.) = 47° 0'; [P∞] : [P∞] = 79° 20'; oP : ∞P = 92° 35'. Cleavage perfect parallel to ∞P∞. (Schabus). By dry distillation, the salt yields sulphurous oxide, inflammable gas, water, and neutral methylic sulphate, leaving sulphate of barium slightly coloured with charcoal.—An isomer of this salt is obtained in very thin prisms, when wood-spirit which has absorbed the vapour of sulphuric anhydride is diluted with water and saturated with baryta-water.

The *calcium-salt*, $(CH^3)^2Ca''(SO^4)^2$, forms anhydrous, very deliquescent octahedrons.

The *lead-salt*, $(CH^3)^2Pb''(SO^4)^2$, crystallises in long prisms containing 1 at. water, or sometimes in tables containing 2 at. water. The crystals are very soluble and deliquescent.

The *potassium-salt*, $CH^3KSO^4.H^2O$, forms rhombic, very deliquescent, monoclinic tables, exhibiting the faces oP . −P . ∞P . [P∞]. Axes, $a : b : c = 0·742 : 0·779 : 1$. Angle $b : c = 86° 51'$; ∞P : ∞P (clinod.) = 87° 16'; −P : −P = 99° 15'; [P∞] : [P∞] = 40° 50'. (Schabus.)

The *uranic salt*, $(CH^3)^2(U^2O^2)''(SO^4)^2.H^2O$, obtained by precipitating the barium-salt with uranic sulphate, and evaporating the filtrate in a vacuum, is deposited after some time in very deliquescent crystals.

DIMETHYLIC or NEUTRAL METHYLIC SULPHATE, $(CH^3)^2SO^4$. *Methylsulphuric Ether.* (Dumas and Péligot, Ann. Ch. Phys. [2] lviii. 32.)—Produced by the direct combination of sulphuric anhydride and methylic oxide: $(CH^3)^2O + SO^3 = (CH^3)^2SO^4$; also in the dry distillation of methylsulphates.

It is most readily prepared by distilling 1 pt. of wood-spirit with 8 or 10 pts. of strong sulphuric acid, the mixture being kept in a state of gentle ebullition; washing the oily liquid which condenses in the receiver, with water; agitating it with chloride of calcium; and rectifying it several times over finely-pounded caustic baryta.

Methylic sulphate is a colourless oil, having an alliaceous odour and a density of 1·324 at 22° (Dumas and Péligot); 1·385 at ordinary temperatures (Bödeker, Jahresb. 1860, p. 17). It boils at 188°, under a pressure of 761 millimetres.

It is slowly decomposed by cold, rapidly by boiling *water*, into methylic alcohol and methylsulphuric acid.—When boiled with *alkalis*, it yields methylic alcohol and an alkaline sulphate.—By distillation with fused *chloride of sodium*, it yields methylic chloride and sulphate of sodium; with *benzoate of potassium*, methylic benzoate and sulphate of potassium; with *formate of sodium*, in like mannner, it yields methylic formate; and in contact with *sulphides of alkali-metal*, it is converted into methylic sulphide, $(CH^3)^2S$.

Ammonia converts it into methylic sulphamate (sulphamethylane) and methylic alcohol:

$$(CH^3)^2SO^4 + NH^3 = CH^5NSO^3 + (CH^3)HO.$$

This reaction is totally different from that of ethylic sulphate with ammonia (p. 625).

Octylsulphuric Acid, $(C^8H^{17})HSO^4$. *Caprylsulphuric* or *Sulphocaprylic Acid.* (Bouis, Compt. rend. xxxiii. 144; xxxviii. 935.)—Produced by gradually mixing 2 pts. of octylic alcohol with 1 pt. of strong sulphuric acid, keeping the mixture cool at first, but afterwards assisting the action by a gentle heat. It then separates into two layers, the upper of which, consisting chiefly of octylsulphuric acid, may be diluted with water, and neutralised with carbonate of barium, calcium, or lead.

The pure acid, obtained by decomposing the lead-salt with sulphydric acid, or the barium-salt with sulphuric acid, and evaporating in a vacuum over oil of vitriol, is a limpid, colourless, syrupy, strongly acid liquid, which dissolves very readily in water and alcohol, and dissolves zinc and iron with evolution of hydrogen. It blackens when heated, and its aqueous solution, when boiled, is resolved into octylic alcohol and sulphuric acid.

Octylsulphate of Barium, $(C^8H^{17})^2Ba''(SO^4)^2$, is obtained in fine, flexible, nacreous crystals containing 2 at. water, by cooling its solution, or leaving it over oil of vitriol; the crystals, merely freed from mother-liquor by pressure between filter-paper, contain 3 at. water. It is very soluble in water, has an extremely bitter taste, and leaves a strongly saccharine aftertaste. The solution is decomposed by boiling, and the dry salt by heating to 100°, or by prolonged keeping in a vacuum.

The *calcium-salt* crystallises in colourless tables, bitter and soapy to the touch.

The *neutral lead-salt* crystallises readily: its solution is acid to test-paper. By digestion with massicot, it yields a colourless alkaline solution, containing a *basic lead-salt*, which, on exposure to the air, becomes covered with pellicles of lead-carbonate, and is reconverted into the neutral salt.

The *potassium-salt*, $C^8H^{17}KSO^4.H^2O$, is white, nacreous, permanent in the air, very soluble in water and in alcohol. When heated, it begins to fuse, and burns with a bright flame without carbonisation. It decomposes at temperatures above 100°.

Phenylsulphuric Acid, $C^6H^6SO^4 = (C^6H^5)HSO^4$. *Sulphophenic* or *Sulphophenylic Acid*. (Laurent, Ann. Ch. Phys. [3], iii. 203.—Freund, Ann. Ch. Pharm. cxx. 76; Jahresb. 1861, p. 617.)—Prepared by treating phenol with excess of strong sulphuric acid; diluting with water after about twenty-four hours; saturating the solution with carbonate of barium; filtering, evaporating, and purifying the crystallised barium-salt thus obtained by recrystallisation from alcohol; and decomposing it with an equivalent quantity of sulphuric acid (Laurent).—Or the barium-salt may be converted into a cupric salt by double decomposition with cupric sulphate, and the cupric salt decomposed by sulphydric acid. (Freund.)

Phenylsulphuric acid may be obtained, by evaporation in a vacuum over oil of vitriol, in slender needle-shaped crystals (Laurent obtained it only as a syrup). The recently prepared solution yields, by distillation, first water containing phenol, then pure phenol, together with sulphurous anhydride; and leaves a carbonaceous residue, the acid being first resolved into phenol and sulphuric acid, ($C^6H^6SO^4 + H^2O = C^6H^6O + H^2SO^4$), which is subsequently reduced to sulphurous acid by the organic matter present. (Freund.)

Phenylsulphates, $C^6H^5MSO^4$ and $(C^6H^5)^2M''(SO^4)^2$.—The *ammonium-salt*, $2C^6H^5(NH^4)SO^4.H^2O$, crystallises in scales.—The *barium-salt*, $(C^6H^5)^2Ba''(SO^4)^2.3H^2O$, crystallises in spherical groups of microscopic needles, which give off their water of crystallisation at 100°, and yield phenol by dry distillation. (Laurent.)

The *cupric salt*, $C^{12}H^{10}Cu''S^2O^8$, separates from a concentrated aqueous solution on cooling, or by spontaneous evaporation, in greenish-blue permanent crystals containing 6 at. water; and the dark-green mother-liquor yields, by further concentration, crystals containing 4 at. water. The mother-liquor remaining after the hexhydrated crystals had separated by spontaneous evaporation, once yielded, after some time, probably in consequence of depression of temperature, well-defined efflorescent crystals having the colour of blue vitriol, and containing 10 at. water. (Freund.)

The *cobalt-salt*, $C^{12}H^{10}Co''S^2O^8.8H^2O$, forms beautiful crystals, having the colour of neutral cobalt-sulphate, permanent in the air, easily soluble in water and in alcohol, and giving up part of their water (19 per cent.) at 180°.—The *nickel-salt*, $C^{12}H^{10}Ni''S^2O^8.8H^2O$, forms emerald-green crystals, which are permanent in the air, dissolve in water and in alcohol, and acquire a canary-yellow colour when dehydrated. (Freund.)

The *magnesium-salt* forms white needle-shaped crystals, soluble in water and in alcohol.

The *potassium-salt*, $C^6H^5KSO^4.H^2O$, forms small silky crystals, soluble in water and in alcohol.

The *silver-salt*, dried over oil of vitriol, is anhydrous, very soluble in water and in alcohol, and crystallises indistinctly. (Freund.)

Paraphenylsulphuric Acid, $C^6H^6SO^4$, called *Oxyphenylsulphuric Acid* by R. Schmitt (Ann. Ch. Pharm. cxx. 129; Jahresb. 1861, p. 623.)—This acid is produced: 1. By passing a rapid stream of nitrous acid vapour into a hot saturated solution of phenylsulphamic (sulphanilic) acid (p. 477):

$$C^6H^7NSO^3 + HNO^2 = C^6H^6SO^4 + H^2O + N^2.$$

2. By heating diazophenylsulphurous acid to 80°:

$$C^6H^4N^2SO^3 + H^2O = C^6H^6SO^4 + N^2.$$

If this decomposition be allowed to take place in a vessel from which air is excluded, and the resulting liquid be concentrated over the water-bath, in a flask into which a stream of carbonic acid gas is continually passed, the acid is obtained as a light-brown uncrystallisable syrup. (Schmitt.)

Paraphenylsulphuric acid decomposes carbonates, and forms salts which are very soluble in water, and can be obtained in the crystalline state only by evaporating their solutions to dryness.—The *barium-salt*, $C^{12}H^{10}Ba''S^2O^8.xH^2O$, requires a strong heat to decompose it. When heated with solid potash, it forms sulphate of potassium, and gives off phenol.—The *silver-salt*, $C^6H^5AgSO^4$, bears in the dry state a tolerably high temperature without decomposition. Both these salts have a yellowish or brownish colour. (Schmitt.)

Dibromophenylsulphuric Acid, $C^6H^4Br^2SO^4$, is produced by boiling diazodibromophenylsulphurous acid (*infra*) with water. By saturating its aqueous solution with carbonate of ammonium, adding chloride of barium, and recrystallising the resulting precipitate, the barium-salt is obtained in needle-shaped crystals. (Schmitt.)

Appendix to Phenylsulphuric Acid.

PHENYLSULPHUROUS ACID, $(C^6H^5)HSO^3$.—To the description of this acid already given (p. 564), we have to add the following results obtained by Freund (Ann. Ch. Pharm. cxx. 76):—Pure benzene (prepared by distilling calcic benzoate), left in contact with frequently-renewed quantities of pure strong sulphuric acid at ordinary temperatures, and repeatedly shaken, dissolves completely, without evolution of sulphurous oxide; and the product diluted with water also dissolves perfectly, forming a clear liquid; and by neutralising this liquid with carbonate of barium, filtering, evaporating to dryness, redissolving in water, and again concentrating, pure *phenylsulphite of barium* is obtained, in transparent nacreous laminæ or tables, containing $C^{12}H^{10}Ba''S^2O^6.2H^2O$. This salt is slightly soluble in alcohol, and effloresces over oil of vitriol, but not on mere exposure to the air.—*Cupric phenylsulphite*, $C^{12}H^{10}Cu''S^2O^6.6H^2O$, prepared by decomposing the barium-salt with cupric sulphate, evaporating the filtrate to dryness, and redissolving in alcohol, crystallises from a hot concentrated alcoholic or aqueous solution, on cooling, in large, thin, tabular, light-blue crystals, permanent in the air; by spontaneous evaporation of the aqueous solution, also in well-defined crystals.—The *silver-salt*, $C^6H^5AgSO^3.8H^2O$, produced by precipitating the barium-salt with sulphate of silver, forms tabular crystals, soluble in water and in alcohol.

Phenylsulphurous acid, obtained by decomposing the cupric salt with sulphuretted hydrogen, crystallises by evaporation, in slender very deliquescent needles. The aqueous solution, when distilled, begins to decompose as soon as it attains a syrupy consistence, giving off sulphurous oxide, benzene, and sulphobenzide (p. 486), which condenses in the crystalline form; the distillate also contains sulphuric and undecomposed phenylsulphurous acids, while a black liquid, or a light, shining, carbonaceous mass, is left behind, according to the strength and duration of the heating. Phenylsulphurous acid is therefore decomposed by distillation, partly by assumption of 1 at. water, into benzene and sulphuric acid:

$$C^6H^6SO^3 + H^2O = C^6H^6 + H^2SO^4;$$

partly into sulphobenzide and sulphuric acid:

$$2C^6H^6SO^3 = C^{12}H^{10}SO^2 + H^2SO^4.$$

At the same time, a secondary decomposition takes place, attended with elimination of sulphurous acid and separation of carbon. (Freund.)

Paraphenylsulphurous Acid.—This name may be applied to an uncrystallisable modification of phenylsulphurous acid, obtained—according to R. Schmitt (Ann. Ch. Pharm. cxx. 129), by whom it is inappropriately termed "phenylsulphuric acid" (*Phenylschwefsäure*)—by heating diazophenylsulphurous acid (*infra*) with absolute alcohol under pressure.—Its *barium-salt*, $C^{12}H^{10}Ba''S^2O^6.xH^2O$, is soluble in water, slightly soluble in alcohol, gives off its water of crystallisation at 110°, and decomposes at a higher temperature.—The *lead-salt*, $C^{12}H^{10}Pb''S^2O^6.xH^2O$, is a colourless crystalline mass, easily soluble in water, very slightly soluble in alcohol.

Dibromophenylsulphurous Acid, $C^6H^4Br^2SO^3$ (Schmitt's *Dibromophenylschwefsäure*), is produced by boiling diazodibromophenylsulphurous acid with absolute alcohol under pressure. By evaporation it is obtained as a brown liquid, which solidifies after some time to a crystalline mass; and by precipitating its solution with acetate of lead, decomposing the lead-salt with sulphuretted hydrogen, and evaporating, it may be obtained in needle-shaped crystals containing 1 at. water; these crystals melt at 84°—86°, without loss of water, and decompose at a higher temperature.

The salts of this acid resemble the dibromosulphanilates (p. 478) in solubility.—The *barium-salt*, $C^{12}H^6Ba''Br^4S^2O^6.xH^2O$, obtained by precipitation, crystallises from hot water in long needles, sparingly soluble in cold water and in alcohol; it gives off its water at 100°, but does not decompose even at 200°. By dry distillation, it gives off water, sulphurous oxide, and an oil having the odour of bromobenzene.—The *lead-* and *silver-salts* crystallise in needles slightly soluble in water.—The *potassium-salt* forms easily soluble needles. (Schmitt, *loc. cit.*)

Diazophenylsulphurous Acid, $C^6H^4N^2SO^3$ (Schmitt, *loc. cit.*). *Diazophenylschwefelsäure.*—This acid is produced by the action of nitrous acid on sulphanilic acid (p. 478), $2C^6H^7NSO^3 + N^2O^3 = 2C^6H^4N^2SO^3 + 3H^2O$. It is insoluble in cold water, but dissolves easily in water at 60°—70°, and separates, by rapid cooling, in small colourless needles. It is insoluble in cold alcohol, and is decomposed by boiling alcohol, with evolution of nitrogen. Its aqueous solution is very unstable, and gives off nitrogen continuously. When heated to 100°, it decomposes with explosive violence, leaving a brown woolly substance. Gaseous ammonia decomposes it with explosion. It is decomposed by *hydriodic* and *hydrobromic acids*, with evolution of nitrogen; and by *sulphydric acid*, with evolution of nitrogen, separation of sulphur, and formation of sulphanilic acid:

$$2C^6H^4N^2SO^3 + 3H^2S = 2C^6H^7NSO^3 + S^3 + N^2.$$

When boiled with *alcohol* of 90 per cent., it yields aldehyde, paraphenylsulphurous acid, and paraphenylsulphuric acid; but when it is heated with absolute alcohol, under pressure, only the first two products are obtained, thus:

$$C^6H^4N^2SO^3 + C^2H^6O = C^6H^6SO^3 + C^2H^4O + N^2.$$

Diazodibromophenylsulphurous acid, $C^6H^2Br^2N^2SO^3$, is produced by the action of nitrous acid on bromosulphanilic acid (p. 479). It forms yellowish-white scales, which are permanent at 100°, but decompose with detonation at a higher temperature. It dissolves in alcohol, but not without detonation; is nearly insoluble in cold water, easily soluble in hot water; but decomposes in aqueous solution at the boiling heat, with evolution of nitrogen. Its reactions are similar to those of diazophenylsulphurous acid.

Tetrylsulphuric Acid, $(C^4H^9)HSO^4$. *Butylsulphuric Acid. Sulphobutylic Acid.* (Wurtz, Compt. rend. xxxv. 310.)—Produced by mixing tetrylic alcohol with an equal volume of strong sulphuric acid, taking care that the mixture does not become hot. After about twenty-four hours the action is complete, and a product is obtained perfectly soluble in water. The solution, saturated with carbonate of potassium, and evaporated to dryness over the water-bath, yields a mixture of sulphate and tetrylsulphate of potassium.

The tetrylsulphate, $C^4H^9KSO^4$, extracted from the mixture by boiling absolute alcohol, crystallises on cooling, in shining anhydrous laminæ, which when dry have a nacreous lustre, and are unctuous to the touch. The salt distilled with cyanate of potassium yields a mixture of tetrylic cyanate and cyanurate.

Tritylsulphuric Acid, $(C^3H^7)HSO^4$. *Propylsulphuric* or *Sulphopropylic Acid.* (Chancel, Compt. rend. xxxvii. 410.)—The potassium-salt of this acid, $C^3H^7KSO^4$, prepared from tritylic alcohol in the same manner as the preceding, crystallises on cooling from alcoholic solution, in anhydrous very slender needles, extremely soluble in water.

Hyposulphurous Compounds.

HYPOSULPHUROUS OR THIOSULPHURIC ACID, $H^2S^2O^3$; called also *Dithionous Acid*, and *Sulphuretted Sulphurous Acid.* (Gay-Lussac, Ann. Chim. lxxxv. 199.—Herschel, Ed. Phil. J. i. 8, 296; ii. 154.—Kessler, Pogg. Ann. lxxxiv. 274.—Vohl, Ann. Ch. Pharm. xciv. 237.—Slater, Chem. Gaz. 1856, p. 369.)—This acid is scarcely known in the free state, since, when liberated from any of its salts by the action of a stronger acid, it is almost immediately resolved into sulphurous acid and sulphur: $H^2S^2O^3 = H^2SO^3 + S$. According to H. Rose, however (*Traité de Chimie analytique*, i. 475), the decomposition is never complete unless the quantity of hyposulphite operated upon is very small; and the liquid, if filtered from the deposited sulphur, even after several weeks, still exhibits the reactions of hyposulphurous acid. According to Flückinger (J. Pharm. [3], xlvi. 453; Jahresb. 1863, p. 149), small quantities of this acid are often found in flowers of sulphur, in precipitated sulphur, in sulphur which has been crystallised from carbonic disulphide, and even in roll-sulphur. Flückinger finds also that it is produced by the action of aqueous sulphurous acid on pure sulphur, even at ordinary temperatures, but more readily at 80° or 90° in a sealed tube. When a mixture of finely-divided cadmium, sulphide of cadmium, and sulphur, moistened with absolute alcohol, was treated with sulphurous acid, sulphuretted hydrogen then passed into the filtrate after the sulphurous acid had evaporated, and the excess of sulphuretted hydrogen removed, the liquid after five months still exhibited the reactions of hyposulphurous acid,—a fact which confirms H. Rose's statement as to the stability of that acid in dilute solutions.

Hyposulphites.—These salts may for the most part be regarded either as analogous to the formates ($MHCO^2$), and represented by the formulæ $MHSO^2$ and $M''H^2S^2O^4$, or as hydrated thiosulphates, $\left.\begin{matrix}M^2\\ \text{or } M''\end{matrix}\right\}SO^3.H^2O$, derived from sulphates, $\left.\begin{matrix}M^2\\ \text{or } M''\end{matrix}\right\}SO^4$, by the substitution of S for O:

$$M^2S^2O^3.H^2O \quad = \quad 2MHSO^2$$
$$M''S^2O^3.H^2O \quad = \quad M''H^2S^2O^4.$$

The former view is in accordance with the fact established by H. Rose, that nearly all hyposulphites contain at least one atom of hydrogen; also with the formation of hyposulphites by the action of sodium, zinc, or iron on aqueous sulphurous acid, just as sodic formate is produced by the action of sodium on carbonic acid (ii. 683):

$$\underset{\substack{\text{Sulphurous}\\ \text{acid.}}}{2H^2SO^3} + Na^2 = \underset{\substack{\text{Sodic hypo-}\\ \text{sulphite.}}}{NaHSO^2} + \underset{\substack{\text{Acid sodic}\\ \text{sulphite.}}}{NaHSO^3} + H^2O.$$

$$\underset{\substack{\text{Carbonic}\\ \text{acid.}}}{2H^2CO^3} + Na^2 = \underset{\substack{\text{Sodic}\\ \text{formate.}}}{NaHCO^2} + \underset{\substack{\text{Acid sodic}\\ \text{carbonate.}}}{NaHCO^3} + H^2O.$$

But, on the other hand, hyposulphate of lead contains no water of crystallisation, and may be rendered completely anhydrous by heating to 100° (Pape, Jahresb. 1864, p. 57): it cannot, therefore, be regarded as analogous to a formate, but must be represented by the formula $Pb''S^2O^3$. The potassium-salt appears also to be capable of crystallising with less than 1 at. water. The dibasic formula M^2SO^3 is also more in accordance with the tendency of hyposulphurous acid to form double salts.

Hyposulphites are produced:—*α*. By passing sulphurous oxide through a solution of an alkaline sulphide, the reaction being accompanied by deposition of sulphur; *e.g.*:

$$2Na^2S + 3SO^2 = 2Na^2S^2O^3 + S$$
$$2Na^2S^5 + 3SO^2 = 2Na^2S^2O^3 + S^9;$$

or, better, by digesting or boiling sulphur with a solution of an alkaline sulphite; thus:

$$Na^2SO^3 + S = Na^2S^2O^3.$$

β. By boiling sulphur with a solution of alkaline hydrate, an alkaline pentasulphide being formed at the same time; thus with calcic hydrate:

$$3CaH^2O^2 + S^{12} = CaS^2O^3 + 2CaS^5 + 3H^2O.$$

By exposing the resulting solution to the air till it becomes colourless, the pentasulphide is further resolved into sulphur and hyposulphite:

$$CaS^5 + O^3 = CaS^2O^3 + S^3.$$

In this manner hyposulphites are obtained from gas-lime refuse and ball-soda refuse, which contain sulphide of calcium.

γ. By the action of certain metals on aqueous sulphurous acid (*supra*).

δ. According to Rathke and Zschiesche (J. pr. Chem. xcii. 141), hyposulphites are produced, together with hyposulphates (dithionates), when selenium is dissolved in an alkaline sulphite. By quickly evaporating such a solution, recently prepared and saturated, a crystalline mass is obtained, coloured red by separated selenium, and consisting mainly of alkaline sulphite mixed with hyposulphate; and the solution of these crystals, freed from selenium by filtration, and evaporated (even in an atmosphere of hydrogen), again deposits selenium, and afterwards a mixture of sulphite and hyposulphite. The mother-liquor of the first crystals also leaves, when evaporated, a certain quantity of selenium, and a crystalline mass consisting of a small quantity of sulphite, and a large quantity of hyposulphite together with separated sulphur.

The hyposulphites of the alkali-metals, alkaline earth-metals, and magnesium are soluble in water. That of barium, however, is only slightly soluble, and may be obtained, as a crystalline precipitate, by mixing the solutions of baric chloride and sodic hyposulphite.

Solutions of hyposulphites dissolve chloride, iodide and bromide of silver, mercurous chloride, iodide of lead, sulphate of calcium, and sulphate of lead. Mercuric iodide dissolves in cold aqueous hyposulphite of sodium, and the solution when heated deposits red sulphide of mercury free from iodide.—Cuprous and cupric hydrates dissolve in the same salt at ordinary temperatures, and are precipitated on heating (Field, Chem. Soc. Qu. J. xvi. 28; Jahresb. 1863, p. 179).—According to Diehl (Jahresb. 1860, p. 78), the ferrocyanides of zinc, manganese, cobalt, nickel, cadmium, and tin are insoluble in aqueous hyposulphite of sodium, whereas those of potassium, copper, lead and silver, and the ferricyanides of silver and mercury, are dissolved by it. The white precipitate formed by ferrocyanide of potassium in ferrous salts is not dissolved by it; the Prussian-blues are converted into a white compound.—The alkaline cyanides and ferrocyanides are converted, by fusion with the hyposulphites of potassium and sodium, into sulphocyanates. (Fröhde, p. 514.)

Solutions of hyposulphites give, with *mercuric, plumbic* and *argentic salts*, white precipitates of metallic hyposulphites, which speedily become yellow, brown, and black, especially if heated, owing to the resolution of the hyposulphite into metallic sulphide and sulphuric acid:

$$Ag^2SO^3.H^2O \quad = \quad Ag^2S \ + \ H^2SO^4.$$

With *stannous chloride* they give off a brown, and with *mercurous nitrate, nickel-salts,* and *cobalt-salts,* a black precipitate of metallic sulphide.—With *ferrous salts* they give no precipitate, even at the boiling heat, under the ordinary atmospheric pressure; but by prolonged heating to 130°—140° in sealed tubes, the iron is completely precipitated as sulphide.—*Zinc* is but partially precipitated even at 120°, and *manganese* not at all, unless iron is also present, in which case a manganiferous sulphide of iron is thrown down under increased pressure (Wolcott Gibbs, Sill. Am. J. xxxvii. 346; Jahresb. 1864, p. 183).—When a soluble hyposulphite is boiled with an *aluminium-salt,* alumina and sulphur are precipitated, sulphurous oxide is evolved, and the acid of the aluminium-salt remains in solution combined with the base of the hyposulphite (Chancel, i. 185); *e.g.*:

$$3Na^2S^2O^3 \ + \ Al^2(SO^4)^3 \quad = \quad Al^2O^3 \ + \ S^3 \ + \ 3SO^2 \ + \ 3Na^2SO^4.$$

According to Gibbs, the precipitation is accelerated by heating under increased pressure, and the precipitated alumina is then insoluble in dilute sulphuric acid, and nearly insoluble in cold concentrated hydrochloric acid.

Hyposulphites heated with *hydrochloric acid,* give off sulphurous oxide and deposit sulphur, which in this case is yellow, not white, as it usually is when precipitated from solution. When treated with *iodine,* they form a metallic iodide and a tetrathionate, thus:

$$2Ba''S^2O^3 \ + \ I^2 \quad = \quad Ba''I^2 \ + \ Ba''S^4O^6.$$

These two reactions distinguish hyposulphurous from sulphurous acid. The reaction with iodine is sometimes used for the volumetric estimation of that substance (Brown, Chem. Soc. Qu. J. x. 71).—Hyposulphites treated with *hypochlorite of sodium,* or with chlorine in presence of water, are completely converted into sulphates even at ordinary temperatures; *e.g.*:

$$Na^2S^2O^3 \ + \ Cl^8 \ + \ 5H^2O \quad = \quad 8HCl \ + \ 2NaHSO^4.$$

Hyposulphites are oxidised by *permanganate of potassium,* and converted into sulphates and hyposulphates: in an alkaline solution, 1 at. hyposulphite of sodium takes up exactly 4 at. oxygen, and is converted into sulphate: $Na^2S^2O^3.H^2O + O^4 = 2NaHSO^4$ (Péan-de-St-Gilles, Ann. Ch. Phys. [3], lv. 374; Jahresb. 1858, p. 583). Neutral chromates are not decomposed by sodic hyposulphite even at the boiling heat; but *acid chromates* are reduced to neutral chromates, especially on heating, with separation of CrO^2. (E. Kopp, Jahresb. 1864, p. 233.)

Hyposulphites treated with *zinc* and *hydrochloric acid,* yield free sulphur and a large quantity of sulphydric acid. This reaction is extremely delicate, serving, according to E. J. Reynolds (Chem. News, viii. 283) for the detection of $\frac{1}{500.000}$th part of sodic hyposulphite in a solution, if a piece of paper moistened with acetate of lead be exposed to the evolved sulphydric acid.

All hyposulphites are decomposed by heat, those of the alkali-metals into a polysulphide and a sulphate; *e.g.*:

$$4Na^2S^2O^3 \quad = \quad 3Na^2SO^4 \ + \ Na^2S^5.$$

Those which contain water of crystallisation (*e.g.*, the potassium-, sodium-, and barium-salts) do not give it up till they are heated nearly to the point (about 220°) at which decomposition begins. (Pape, Jahresb. 1864, p. 57.)

To detect hyposulphurous acid in presence of sulphydric acid or a soluble sulphide, the solution is made neutral and precipitated by a zinc-salt, the sulphide of zinc filtered off, and the filtrate tested for hyposulphurous acid.

Soluble hyposulphites, especially the sodium-salt, are much used for fixing photographic pictures, which they effect by dissolving out the chloride of silver which has not been acted upon by light. The sodium-salt is also largely employed as an antichlore, for removing the last traces of chlorine from bleached fabrics. On the use of soluble hyposulphites as mordants in calico-printing, see E. Kopp (Dingl. pol. J. cl. 383).

Hyposulphite of Ammonium, $3(NH^4)^2S^2O^3.H^2O$ (Rammelsberg), is obtained by decomposing the calcium-salt with carbonate of ammonium, and separates, by evaporation, in very deliquescent needles or rhombic plates.

Hyposulphite of Barium, $Ba''S^2O^3.H^2O$ or $Ba''H^2S^2O^4$, is obtained, by mixing the solution of the sodium-salt with acetate of barium, as a white precipitate, the separation of which may be completed by addition of alcohol. It retains its water of crystallisation with great tenacity (H. Rose, Pogg. Ann. xxi. 437); gives it off at 215°, and decomposes at 220°—225° (Pape). The anhydrous salt, when heated to redness, gives off sulphur, and leaves a residue of sulphide, sulphite, and sulphate of barium (Rammelsberg, Pogg. Ann. lvi. 300):

$$6Ba''S^2O^3 = Ba''S + 2Ba''SO^3 + 3Ba''SO^4 + S^4.$$

Hyposulphite of Cadmium, obtained by mixing the solutions of cadmic sulphate and baric hyposulphite, is extremely soluble in water and in alcohol, and when concentrated by evaporation decomposes before solidifying.

Hyposulphite of Calcium, $Ca''S^2O^3.6H^2O$, or $Ca''H^2S^2O^4.5H^2O$.—This salt is usually prepared by boiling sulphur with milk of lime, and passing sulphurous acid gas into the solution of calcic sulphide thereby produced, till it becomes colourless and neutral:

$$2Ca''S + 3SO^2 = S + 2Ca''S^2O^3.$$

On evaporating the solution, at a temperature below 60°, the hyposulphite of calcium crystallises out (Herschel). This process is used on the large scale.

The sulphide of calcium contained in soda-waste or gas-lime may be converted into hyposulphite and sulphite by atmospheric oxidation. Messrs. Townshend and Walker employ for this purpose the soda-waste obtained in the lixiviation of crude soda (i. 793; v. 325), which contains a considerable quantity of insoluble calcic sulphide. The oxidation is effected by exposing the waste, in a state of dampness, to the air for some days, occasionally turning it over and sprinkling it with water, or with solution of calcic sulphide. When fully oxidised and lixiviated with water, it yields a solution of calcic hyposulphite and sulphite, the former salt predominating. If the product is lixiviated before the oxidation is complete, a yellow solution is formed, containing sulphide of calcium as well as sulphite and hyposulphite. The complete oxidation may then be effected by causing the yellow solution to percolate slowly through a tower filled with lumps of coke, and having openings at the lower part to admit the air. The sulphite and hyposulphite of calcium thus produced may be obtained in the solid form by evaporation, or merely brought down to the state of concentrated solution, and in either case used as an antichlore. Or the solution may be mixed with sulphate of sodium, whereby a solution of sodic sulphite and hyposulphite is obtained, together with a precipitate of calcic sulphate containing small quantities of sulphite and hyposulphite. This precipitate, dried at a temperature not exceeding 100° C., constitutes the product called "precipitated antichlore." It has been found very valuable in the manufacture of paper, as the hydrated calcic sulphate gives weight and body, while the sulphite and hyposulphite destroy any chlorine present in the paper-pulp (see Richardson and Watts's *Chemical Technology*, vol. i. pt. iii. p. 39).—A somewhat similar process has been patented by Jullion (*ibid.* p. 42), who however subjects the calcic sulphide contained in soda-waste or gas-lime only to partial oxidation, whereby he obtains a yellow solution called "sulphuretted hyposulphite of lime," consisting chiefly of calcic sulphide and hyposulphite. This solution may be decomposed by a strong acid, whereby sulphur is precipitated, and a mixture of sulphurous and sulphydric acid gases is given off, which may be utilised in various ways; or the solution may be treated with sulphurous acid gas, whereby sulphur is precipitated, and the whole of the calcic sulphide converted into hyposulphite.

Hyposulphite of calcium may also be prepared by decomposing chloride of calcium with hyposulphite of sodium, in hot concentrated solution. The liquid, as it cools, deposits a large quantity of sodic chloride; and if it be then concentrated at a temperature below 50°, and allowed to cool to 30°, after all the sodic chloride has separated out, it yields crystals of pure calcic hyposulphite. (Kessler.)

Hyposulphite of calcium crystallises in large, eight-sided, triclinic prisms, exhibiting the combination $\infty P'_{,} . \infty_{,}P' . \infty\breve{P}\infty . \infty\bar{P}\infty . oP$ (Kopp's *Krystallographie*, 2te Auflage, p. 239). It is easily soluble in water, and is decomposed, on heating the solution to 60°, into sulphate of calcium and free sulphur.

Hyposulphite of Cobalt, $Co''S^2O^3.6H^2O$ or $Co''H^2S^2O^4.5H^2O$.—Obtained, as a dark-red crystalline mass, by mixing the solutions of cobalt-sulphate and strontium-hyposulphite, and evaporating. (Rammelsberg.)

Hyposulphites of Copper.—Neither cupric nor cuprous hyposulphite is known in the separate state; but some double salts of cuprous hyposulphite with alkaline hyposulphites have been obtained by mixing the solutions of the latter with cupric salts. Their solutions are colourless, have a sweet taste, yield with alkalis a precipitate of cuprous oxide, and are decomposed by heating with acids.—A *potassium-salt*, $Cu^2K^2S^4O^6.2H^2O$, separates on mixing the solutions of potassic hyposulphite and cupric sulphate or acetate, as a yellow precipitate, which soon turns black, from formation of sulphide of copper, and is completely decomposed by water into sulphide of copper, sulphurous acid, and sulphuric acid. The solution of this double salt in hyposulphite of potassium deposits, on addition of alcohol, an oily liquid, which solidifies to a white salt having the composition $Cu^2K^6S^8O^{12}.3H^2O$ (Rammelsberg).—A *sodium-salt*, containing $Cu^6Na^4S^{10}O^{15}.5H^2O$ (Lenz), is obtained, like the first-mentioned potassium-salt, as a yellow crystalline precipitate, which it is best to wash with water containing acetic acid. From its solution in hyposulphite of sodium, alcohol throws down a white salt, $Cu^2Na^6S^8O^{12}.2H^2O$.—According to Schütte (Compt. rend. xlii. 1257), a salt having the composition $(Cu^2; Cu'')Na^2S^4O^6.NH^3$, is obtained, in small violet needles, by adding a concentrated solution of sodic hyposulphite to an ammoniacal solution of a cupric salt. The crystals are permanent in the air, give off ammonia at 100°, and are decomposed at a stronger heat, also by cold water.—H. Peltzer (Ann. Ch. Pharm. cxxvi. 351; cxxviii. 187; Jahresb. 1863, p. 277) describes a salt having the composition $Cu^2Cu''Na^4S^8O^{12}.2NH^3$, as separating in dark-blue needles or prisms, from a solution of cupric sulphate and sodic hyposulphite in ammonia, or as a violet powder on mixing equal volumes of the solutions of cupric sulphate and sodic hyposulphite both saturated with ammonia. It is decomposed but not dissolved by hot water, dissolves in ammonia and in sodic hyposulphite, and, when heated with potash-ley, yields a precipitate of cupric and cuprous oxides. Acetic acid dissolves the salt with yellowish-green colour, and alcohol throws down from the solution, first a white, then a canary-yellow, tolerably permanent salt, not containing ammonia. Hyposulphite of sodium produces in the acetic solution, after a while, a heavy white precipitate of a cuprous salt containing tetrathionic acid. A strong solution of silver-nitrate forms, in the same liquid, first a grey precipitate, which soon redissolves; then a precipitate which dissolves with blue colour in ammonia, quickly decomposes with formation of silver-sulphide, and gives the reactions of cupric oxide, silver, and hyposulphurous acid.

Hyposulphites of Gold.—*Sodio-aurous hyposulphite*, $AuNa^3S^4O^6.2H^2O$, is produced by mixing the solutions of auric chloride and sodic hyposulphite, and adding alcohol. Its aqueous solution yields, with chloride of barium, a gelatinous precipitate of *bario-aurous hyposulphite*, $Au^2\overset{''}{Ba}{}^3S^8O^{12}$; and this salt, decomposed by sulphuric acid, yields uncrystallisable hydrated *aurous hyposulphite*. A *sodio-auric hyposulphite* appears also to be formed by dropping a neutral solution of auric chloride into a solution of sodic hyposulphite (Fordos and Gélis). See Gold (ii. 931).

Hyposulphites of Iron.—The *ferric salt* is not known.—*Ferrous hyposulphite*, $2Fe''S^2O^3.5H^2O$, is produced, together with the sulphite, by dissolving iron in aqueous sulphurous acid. On evaporating the solution, or mixing it with alcohol, the sulphite separates out; and the mother-liquor, when further evaporated, yields crystals of ferrous hyposulphite, which are more stable than those of the sulphite, and may be kept unaltered if excluded from the air. Rammelsberg obtained the salt in small green crystals, mixed with a basic ferric salt, by mixing the solution of ferrous sulphate with hyposulphite of barium or strontium. On attempting to concentrate the salt further in contact with the air, a small quantity of ferric salt is first formed, which then acts upon the hyposulphite, converting it into ferrous tetrathionate, and the latter is resolved by further evaporation into ferrous sulphate, sulphurous acid, and sulphur. (Fordos and Gélis.)

Hyposulphite of Lead, $Pb''S^2O^3$, is a white precipitate, very sparingly soluble in water, but dissolving in alkaline hyposulphites, with formation of double salts. It may be dried at 100° without decomposition; but at a stronger heat, it blackens and gives off sulphurous oxide, and leaves a residue of sulphide and sulphate of lead. When heated in the air, it glows like tinder.

Ammonio-plumbic hyposulphite, $Pb''(NH^4)^4S^6O^9.5H^2O$, separates by spontaneous evaporation from its solution, obtained as above, in rhombic prisms shortened into tables. It dissolves in water without immediate decomposition, but the solution becomes cloudy after a while, from separation of plumbic hyposulphite; when heated, it yields sulphide of lead.—*Bario-plumbic hyposulphite* is a sparingly soluble salt, obtained by precipitating the solution of one of the alkaline double salts with acetate of barium.—*Calcio-plumbic hyposulphite*, $Pb''Ca^2S^6O^9.4H^2O$, is obtained in like manner as a crystallo-granular precipitate.—*Potassio-plumbic hyposulphite*, $Pb''K^4S^6O^9.2H^2O$, is prepared by agitating the recently precipitated lead-salt with a dilute and warm (but not boiling) solution of potassic hyposulphite. On cooling, the entire liquid solidifies to a thick magma of small crystals, which must be purified by expressing the mother-liquor, as they are decomposed by solution in water, the simple lead-salt then separating in crystalline spangles. The double salt dissolves easily in hyposulphite of potassium, and the lead is but slowly precipitated from the solution by sulphuric acid, sulphur being precipitated at the same time; the solution is not precipitated by soluble sulphates.—*Sodio-plumbic hyposulphite* is prepared in a similar manner. The strontio-plumbic salt is not crystalline, but separates from solution as a syrupy mass.

Hyposulphite of Magnesium, $Mg''S^2O^3.6H^2O$ or $Mg''H^2S^2O^4.5H^2O$, is prepared by boiling a solution of magnesic sulphite with sulphur, and evaporating over oil of vitriol. It forms small triclinic crystals, permanent in the air, and easily soluble. When heated, it melts, gives off water, sulphur, and sulphurous acid, and leaves when ignited a mixture of magnesic sulphate and sulphite with pure magnesia. Jullion prepares it by boiling pulverised soda-waste or gas-lime with carbonate of magnesium, whereby carbonate of calcium and insoluble sulphide of magnesium are produced, rendering the latter soluble by boiling it with sulphur or an alkaline polysulphide, and converting the soluble sulphide of magnesium into hyposulphite by treating the solution with sulphurous acid.—*Ammonio-magnesic hyposulphite*, $Mg''(NH^4)^2S^4O^6.6H^2O$, is obtained by decomposing ammonio-magnesic sulphite with hyposulphite of strontium. The concentrated solution becomes turbid when heated, and when cooled below the freezing-point of water, deposits very deliquescent crystals (Kessler).—*Potassio-magnesic hyposulphite*, $Mg''K^2S^4O^6.6H^2O$, is deposited from a hot solution of equivalent quantities of potassic and magnesic hyposulphites, in very soluble deliquescent crystals, which may be obtained of considerable size by immersing previously-formed crystals in the concentrated solution.

Hyposulphite of Manganese is known only in solution, and is produced by decomposing the barium- or strontium-salt with manganous sulphate; also (according to Rammelsberg) by dissolving recently precipitated sulphide of manganese in aqueous sulphurous acid. It is decomposed by evaporation into sulphur and manganous sulphur.

Hyposulphites of Mercury.—*Potassio-mercuric hyposulphite*, $Hg^3K^{10}S^{16}O^{24}$, is produced by dissolving mercuric oxide in hyposulphite of potassium. The liquid becomes warm, and on cooling deposits the double salt in colourless, sparingly soluble prisms. Acids decompose it, separating sulphur and sulphide of mercury. Iodide of potassium does not precipitate mercuric iodide from the solution.—*Ammonio-mercuric hyposulphite*, which is very easily decomposible, is separated from its solution by alcohol in colourless prisms.—The *sodio-mercuric salt* is not crystallisable.

Hyposulphite of Nickel, $Ni''S^2O^3.6H^2O = Ni''H^2S^2O^4.5H^2O$, prepared like the cobalt-salt, separates, by evaporation over oil of vitriol, in green triclinic crystals, which when heated give off water, sulphur, and sulphurous acid, leaving sulphide of nickel.—*Ammoniacal Hyposulphite of Nickel*, $Ni''S^2O^3.4NH^3.6H^2O$, is obtained, as a blue crystalline powder, when the blue ammoniacal solution of the preceding salt is mixed with alcohol. It decomposes quickly when exposed to the air.

Hyposulphites of Platinum.—Neither platinous nor platinic sulphite is known in the separate state.—*Sodio-platinous hyposulphite*, $Pt''Na^6S^8O^{12}.10H^2O$, is produced by dissolving ammonio-platinous chloride in a strong solution of sodic hyposulphite; and may be separated, by addition of absolute alcohol, as a dense, yellow, oily liquid, which gradually solidifies to a yellow crystalline mass. When purified by two more precipitations with alcohol, it forms a yellow noncrystalline mass, very soluble in water. Its solution is decomposed by hydrochloric acid, slowly in the cold, quickly when heated, with deposition of platinous sulphide and evolution of sulphurous oxide. It is not decomposed by caustic soda, or by sulphuretted hydrogen. (Schottländer, Ann. Ch. Pharm. cxl. 200; Bull. Soc. Chim. 1867, i. 403.)

Hyposulphite of Potassium, $K^2S^2O^3$.—This salt, which crystallises with various proportions of water, is prepared by boiling a concentrated solution of potassic sulphites with excess of sulphur, or by adding a hot solution of potassic dichromate by small portions to a hot solution of potassic pentasulphide, waiting after each addition till the separated chromic oxide has acquired a pure green colour (Döpping; Kessler). If the solution obtained by either of these methods be evaporated to 30°, the salt crystallises in very thin four-sided prisms, containing $3K^2S^2O^3.H^2O$. These crystals are very soluble in water, and deliquescent, but insoluble in alcohol. They give off their water at 200°, and the anhydrous salt decomposes, at a higher temperature, into a mixture of 1 at. potassic pentasulphide and 3 at. potassic sulphate. (Rammelsberg.)

The mother-liquor decanted from these prisms yields, if briskly stirred or shaken when cold, a quantity of small granular crystals; and if these be redissolved in the solution from which they have separated, with addition of a little water, the liquid on cooling deposits large colourless crystals, having a rhombic octahedron for their primary form. They contain 13·62 per cent. water, and, according to Kessler, consist of $3K^2S^2O^3.5H^2O$, or $3KHSO^2.H^2O$; according to Döpping, of $2K^2S^2O^3.3H^2O$ or $4KHSO^2.H^2O$. These crystals do not deliquesce in moderately damp air, but effloresce immediately over oil of vitriol, or when heated above 40°. This salt dissolves very easily in water, and with great depression of temperature; the solution is neutral, and remains unaltered even in contact with the air. Sometimes these octahedral crystals separate directly from solution either before or after the prismatic crystals, and they are always formed when an octahedral crystal is immersed in a solution of the salt evaporated at 30°.

Döpping mentions also a prismatic salt containing 8½ per cent. of water, and having the composition $K^2S^2O^3.H^2O$ or $KHSO^2$; this, however, Kessler was not able to obtain.

Plessy's salt, $K^2S^2O^3.2H^2O = 2KHSO^2.H^2O$, is regarded by Kessler as identical with the octahedral salt.

The compound $K^2S^2O^3.Hg''Cy$ was once obtained by Kessler, on mixing the solutions of equivalent quantities of potassic hyposulphite and mercuric cyanide, adding alcohol after a crystalline precipitate (probably consisting of potassio-mercuric hyposulphite and potassio-mercuric cyanide) had separated, and evaporating the mother-liquor in a vacuum. It crystallises in large four-sided prisms, which give off 2 per cent. water over oil of vitriol.

Hyposulphite of Silver.—This salt, on account of its extreme instability, is scarcely known in the separate state; but it forms two series of double salts, $R^4Ag^2S^6O^9$ and $RAgS^2O^3$ (R denoting an alkali-metal), prepared by dissolving silver-oxide in an alkaline hyposulphite, or by adding chloride or nitrate of silver to the solution of the alkaline hyposulphite. The salts of the first series dissolve easily in water, and are precipitated therefrom by alcohol; but those of the second series are insoluble or sparingly soluble in water, and separate, in crystalline or pulverulent form, when the salts of the first series are treated with an additional quantity of silver-salt.

These insoluble double salts dissolve easily in ammonia, and the ammoniacal solutions, as well as the aqueous solutions of the double salts of the first series, have an intensely sweet taste. The solutions may be used for silvering; the silver cannot be detected in any of them by hydrochloric acid. All these double salts decompose easily when heated, yielding sulphide and sulphate of silver: hence, in preparing them, the temperature must be kept as low as possible. They are likewise decomposed by alkalis, and by an excess of the alkaline hyposulphite.

Sodio-argentic hyposulphite, $Ag^2Na^4S^6O^9.2H^2O$, is produced by dropping a solution of sodic hyposulphite, with constant stirring, into a solution of silver-nitrate, till a permanent precipitate is formed, and separates in shining laminæ on adding alcohol to the liquid. If, instead of adding alcohol, the addition of the silver-salt be continued, the salt, $AgNaS^2O^3.H^2O$, separates in flocks, which soon become crystalline. (Herschel; Lenz.)

The ammonio-, potassio-, calcio-, strontio-, and plumbo-argentic hyposulphites may be prepared by similar processes. (Herschel.)

Hyposulphite of Sodium, $Na^2S^2O^3.5H^2O$, or $NaHSO^2.2H^2O$.—This salt, which is extensively used as an antichlore, and for fixing photographic pictures, is prepared:—1. By boiling sulphur with soda-ley, and passing sulphurous gas into the solution till it is completely decolorised (p. 630).—2. By igniting sulphate of sodium with charcoal, at a temperature not high enough to fuse the mass, moistening the pulverulent carbonaceous mass with water, and subjecting it to the action of sulphurous acid gas. (Anthon, Pharm. Centr. 1846, p. 414.)

3. By roasting a mixture of sulphur and sodic carbonate in a sulphur-furnace, and adding the product to a boiling solution of sulphur in caustic soda-ley, till the liquid becomes colourless. The clarified solution is then evaporated in iron pans, and the sulphate of sodium which separates is continually taken out. The concentrated liquid deposits hyposulphite of sodium in large pure crystals, and the mother-liquor, mixed with caustic soda, is used for dissolving fresh portions of sulphur. (Jahresb. 1862, p. 664.)

4. By decomposing the hyposulphite of calcium obtained from soda-waste or

gas-lime (p. 632) with carbonate of sodium, and evaporating the filtered solution to the crystallising point. (Richardson and Watts's *Chemical Technology*, vol. i. pt. iv. p. 185.)

Hyposulphite of sodium forms large, well-defined, monoclinic crystals, usually exhibiting the combination $\infty P . [\infty P2] . [\infty P\infty] . oP . [P\infty]$, also with $+ P$ and other faces subordinate. Axes $a : b : c = 2{\cdot}8507 : 1 : 0{\cdot}7825$. Angle $b : c = 76° 2'$; $\infty P : \infty P$ (orthod.) $= 37° 36'$; $[\infty P2] : [\infty P2]$ (orthod.) $= 68° 30'$; $[P\infty] : [P\infty]$ (clinod.) $= 150° 10'$. The crystals have a specific gravity of 1·672 (Buignet), dissolve easily in water, but are insoluble in alcohol. Respecting the specific gravity of its solutions, see Schiff (Jahresb. 1859, p. 41). The aqueous solution cannot be preserved unaltered even in closed vessels, but deposits sulphur, and is partly converted into sulphate of sodium; in contact with the air, it is gradually but completely oxidised to sulphate. The dry salt when heated gives off sulphur, and leaves a mixture of sulphide and sulphate of sodium. The crystals melt in their water of crystallisation at 56°; and if the fusion be performed in a small glass flask, the temperature raised to the boiling-point, the flask then immediately closed, and left to cool quickly on a surface which conducts heat slowly, the salt will remain liquid even at ordinary temperatures; but on immersing the bulb of a thermometer, or dropping a crystal into it, the whole will instantly solidify to a crystalline mass, with a rise of temperature which may amount to 25°. (Böttger.)

A saturated solution of sodic hyposulphite dissolves gypsum with moderate facility at ordinary temperatures, more quickly when gently heated, forming a sodio-calcic hyposulphite, which is precipitated by alcohol, together with excess of sodic hyposulphite, as a heavy oily liquid, which solidifies in needle-shaped crystals. This reaction affords the means of separating sulphate of calcium from sulphate of barium, which is not dissolved by hyposulphite of sodium (Diehl, J. pr. Chem. lxxix. 430; Jahresb. 1860, p. 78). For the reactions with other metallic salts, see p. 631.

Hyposulphite of Strontium, $Sr''S^2O^3.6H^2O$, is prepared like the barium-salt. Alcohol precipitates it from its solution in needles having a silky lustre; but even without the aid of alcohol, it separates in very large crystals. It retains 1 at. water at 180°, and, according to Kessler, the monohydrated salt is likewise obtained in small crystals, by evaporating the solution at or above 50°.

Hyposulphite of Thallium and Sodium, $Tl^4Na^6S^{10}O^{15}.10H^2O$ or $2Tl^2S^2O^3.3Na^2S^2O^3.10H^2O$, is formed by dissolving chloride of thallium in boiling aqueous hyposulphite of sodium, and crystallises in long, silky, interlaced needles,—or from a small quantity of water in small granules (containing an unknown amount of water). At a red heat, it is resolved into sulphide of sodium, sulphate of sodium, and sulphide of thallium. (G. Werther, J. pr. Chem. xci. 385.)

Hyposulphite of Zinc, $Zn''S^2O^3$, is produced by decomposing the barium-salt with sulphate of zinc; also, though with difficulty, by passing sulphurous acid gas into water in which sulphide of zinc is suspended (Rammelsberg); also, together with sulphite of zinc, by dissolving zinc in aqueous sulphurous acid (Mitscherlich). The sulphite crystallises out, and may be completely removed by alcohol; or (according to Berzelius), it may be wholly converted into hyposulphite by digesting the solution with sulphur.

Hyposulphite of zinc cannot be obtained in the crystalline form, but (according to Köne) it is precipitated by anhydrous ether from its aqueous solution, as an oily liquid, which dries up in a vacuum to a gummy deliquescent mass. The concentrated solution is gradually decomposed by exposure to the air, sulphide of zinc being separated, while trithionate of zinc remains in solution: $2Zn''S^2O^3 = Zn''S + Zn''S^3O^6$ (Fordos and Gélis, Compt. rend. xvi. 1070). The solution is also decomposed by heat into sulphuric acid, sulphurous acid, sulphide of zinc, and sulphate of zinc.

Hyposulphite of Zinc-ammonium, $(N^2H^6Zn)''S^2O^3$, is produced by heating hyposulphite of zinc with ammonia, and separates from the solution in slender crystals. (Rammelsberg.)

Dithionic Compounds.

DITHIONIC OR HYPOSULPHURIC ACID, $H^2S^2O^6$. (Welter and Gay-Lussac, Ann. Ch. Phys. [2], x. 312.—Heeren, Pogg. Ann. vii. 55.—Rammelsberg, *ibid.* lviii. 295.)—This acid, discovered by Welter in 1819, is produced as a manganous salt by the action of aqueous sulphurous acid on manganic peroxide:

$$MnO^2 + 2H^2SO^3 = Mn''S^2O^6 + 2H^2O.$$

To prepare the acid, sulphurous oxide gas is passed through water in which finely-divided manganic peroxide is suspended, as long as it continues to be absorbed.

Dithionate and sulphate of manganese are then formed, the dithionate being the principal product, provided the temperature be kept down; at higher temperatures, on the contrary, scarcely anything but sulphate is produced. On adding hydrate of barium to the impure solution of manganous dithionate, hydrate of manganese and sulphate of barium are precipitated, while dithionate of barium remains in solution; and by carefully precipitating the barium with an exactly sufficient quantity of sulphuric acid, a solution of dithionic acid is obtained, which may be concentrated in a vacuum over oil of vitriol, till it attains a specific gravity of 1·347 (Gay-Lussac; Heeren). Gélis (Ann. Ch. Phys. [3], lxv. 222) passes sulphurous oxide through water in which ferric hydrate is suspended, whereby a solution of ferric sulphite, $\mathrm{Fe^2(SO^3)^3}$, is produced; and this solution, when kept in a closed vessel, acquires after some time a light-green colour, and then contains a mixture of ferrous sulphite and dithionate:

$$\overset{\prime\prime\prime}{\mathrm{Fe}}{}^{2}\mathrm{(SO^3)^3} \;=\; \mathrm{Fe''SO^3} + \mathrm{Fe''S^2O^6}.$$

From this solution, the dithionic acid may be separated, by means of hydrate of barium, &c., in the manner above described.

Dithionic acid, when concentrated as highly as possible, is an inodorous, strongly acid, hydrated liquid, of specific gravity 1·347; on attempting to concentrate it further, it is resolved into sulphuric acid and sulphurous oxide: $\mathrm{H^2S^2O^6 = H^2SO^4 + SO^2}$. The dilute acid decomposes in the same manner at higher temperatures. In contact with the air, dithionic acid is gradually oxidised to sulphuric acid; the same change is produced by heating it with nitric acid, chlorine, or manganic peroxide.

Dithionates or Hyposulphates, $\mathrm{M^2S^2O^6}$.—These salts, investigated chiefly by Heeren, are all soluble in water, and are easily prepared by decomposing the barium-salt with the corresponding sulphates. The dithionates of the alkali-metals may also be obtained by dissolving the carbonates in sulphurous acid, boiling the neutral solution with finely pulverised manganic peroxide, and leaving the filtrate to crystallise (C. v. Hauer, J. pr. Chem. lxxx. 229). They are likewise produced, together with hyposulphites, when selenium is dissolved in an alkaline sulphite. (Rathke and Zschiesche, p. 630.)

The dithionates are permanent at ordinary temperatures, both in the solid state and in solution; but when heated, in some cases even at 100°, they give off sulphurous oxide, and leave a residue of neutral sulphate. The solid dithionates are decomposed by strong *sulphuric acid*, at ordinary temperatures, with brisk evolution of sulphurous oxide; the solutions, mixed with *sulphuric* or *hydrochloric acid*, are decomposed at the boiling heat, yielding sulphurous and sulphuric acids, *without separation of sulphur*: this reaction is characteristic of the dithionates. A solution of *potassic manganate* mixed with sulphuric acid is decolorised when boiled with a dithionate. Solid dithionates are decomposed by *phosphoric oxychloride* only when heated. The dry sodium-salt, distilled with *phosphoric pentachloride*, yields a distillate consisting of phosphoric oxychloride and sulphurous chloride, $\mathrm{SOCl^2}$. (Kraut, Ann. Ch. Pharm. cxviii. 95.)

Dithionate of Aluminium separates from its solution by slow evaporation in small crystals, mixed however with a considerable quantity of sulphate. (Heeren.)

Dithionate of Ammonium, $\mathrm{(NH^4)^2S^2O^6.H^2O}$, forms indistinct capillary crystals, very soluble in water, insoluble in alcohol.

Dithionate of Barium, $\mathrm{Ba''S^2O^6}$, prepared as above described, crystallises from the hot saturated solution on cooling, in crystals containing $\mathrm{Ba''S^2O^6.2H^2O}$, which, according to Sénarmont (Jahresb. 1857, p. 142), are trimetric, exhibiting the combination: $\infty\bar{P}\infty \,.\, \infty\breve{P}\infty \,.\, P \,.\, oP \,.\, \frac{1}{2}\bar{P}\infty \,.\, \frac{1}{3}\breve{P}\infty$, and having the axes $a : b : c = 0{\cdot}7199 : 1 : 0{\cdot}6920$; angle $P : \infty\breve{P}\infty = 128° 20'$; $P : oP = 130° 10'$. Rammelsberg also found them to be trimetric with nearly the same ratio of the axes. But, according to the measurements of v. Lang (Wien. Akad. Ber. [2], xlv. 27; Jahresb. 1862, p. 126), made upon well-developed specimens, these dihydrated crystals are monoclinic, exhibiting the combination $oP \,.\, [\infty P\infty] \,.\, +2P\infty \,.\, [P\infty] \,.\, +2P \,.\, [\frac{4}{3}P2] \,.\, [\infty P2] \,.\, +P \,.\, +[P\frac{9}{7}] \,.\, -[P\frac{9}{7}]$. Axes $a : b : c = 1 : 0{\cdot}9343 : 1{\cdot}4030$. Angle $b : c = 110° 37'$; $oP : +P\infty = 108° 22'$; $oP : +P = 103° 45'$; $+P : [P\infty] = 132° 12'$; $[\frac{4}{3}P2] : +2P\infty = 116° 14'$; $[P\frac{9}{7}] : [P\infty] = 118° 41'$; $[P\frac{9}{7}] : +P = 143° 22'$.—A *tetrahydrate*, $\mathrm{Ba''S^2O^6.4H^2O}$, is obtained, by spontaneous evaporation, in distinct, shining, monoclinic crystals, which effloresce quickly on exposure to the air. (Hoeren; Marignac). Dithionate of barium serves, as above mentioned, for the preparation of the other dithionates.

Dithionate of Barium and Magnesium, $\mathrm{Ba''Mg''S^4O^{12}.4H^2O}$, is obtained (according to Schiff, Ann. Ch. Pharm. cv. 239), by precipitating half the barium from baric dithionate with sulphuric acid, saturating the filtrate with magnesia, and evaporating; the double salt then separates on cooling in crystalline geodes, which give off their water completely at 90°.

Dithionate of Barium and Sodium, $\mathrm{Ba''Na^2S^4O^{12}.6H^2O}$, is produced (according to

Schiff), by decomposing the barium-salt with a calculated quantity of sodic sulphate. Kraut (Ann. Ch. Pharm. cxviii. 95), by mixing equivalent quantities of baric and sodic dithionates, obtained large transparent crystals, with curved edges and convex faces, containing $Ba''Na^2S^4O^{12}.4H^2O$, which were permanent in the air, and not resolved into the component salts by recrystallisation; he regards the salt obtained by Schiff as merely a mixture.

Dithionate of Cadmium is obtained, as a crystalline deliquescent mass, by evaporating a solution of the carbonate in dithionic acid (Heeren). It dissolves in ammonia, and the solution on cooling yields a crystalline powder, consisting of the salt $Cd''S^2O^6.4NH^3$ mixed with hydrate of cadmium. (Rammelsberg.)

Dithionate of Calcium, $Ca''S^2O^6.4H^2O$, prepared like the barium-salt, crystallises by spontaneous evaporation in tabular crystals, belonging to the hexagonal system and exhibiting the combination oP : P (*fig.* 239, ii. 139). Length of principal axis = 1·485. Angle P : P (terminal) = 128° 49′; P : P (lateral) = 119° 30′. According to Nörrenberg, they are optically negative. They are permanent in the air, and insoluble in alcohol. (Heeren.)

The *Dithionates of Cerium, Lanthanum*, and *Didymium*, obtained by double decomposition, are crystallisable.

Dithionate of Chromium, $\overset{'''}{Cr^2}S^6O^{18}$, is obtained by dissolving chromic hydrate in aqueous dithionic acid.

Dithionate of Cobalt, $Co''S^2O^6.6H^2O$, separates on evaporation in rose-coloured crystals (Heeren). By treating the solution with ammonia and evaporating, Rammelsberg obtained the salt $Co^2O^3.2S^2O^5.10NH^3$, in small rectangular prisms, which after a while turned brown, and lost their lustre.

Dithionates of Copper.—The normal cupric salt, $Cu''S^2O^6.4H^2O$, forms small, rhombic, efflorescent prisms.—A *basic salt*, $Cu''S^2O^6.3Cu''O.4H^2O$, is obtained, as a blue-green precipitate, on mixing the solution of the normal salt with a small quantity of ammonia (Heeren).—An *ammoniacal cupric dithionate*, $Cu''S^2O^6.4NH^3$, is obtained in thin, tabular, violet-blue prisms with oblique end-faces, by supersaturating the solution of the normal cupric salt with ammonia. (Heeren.)

Dithionates of Iron.—A *basic ferric dithionate* is produced (according to Heeren), by treating recently precipitated ferric hydrate with the aqueous acid, which, however, dissolves but little of it, the greater part being converted into an insoluble, brown, basic salt.—The *ferrous salt*, $Fe''S^2O^6.5H^2O$, obtained by double decomposition, crystallises on evaporation in oblique rhombic prisms, having the colour of ferrous sulphate.

Dithionate of Lead, $Pb''S^2O^6.4H^2O$, prepared by dissolving carbonate of lead in aqueous dithionic acid, forms large crystals belonging to the hexagonal system, isomorphous with the calcium- and strontium-salts, but exhibiting also the face ¼P, occurring hemihedrally with P. The crystals are permanent in the air, optically uniaxial and positive (Nörrenberg). The solution of this salt mixed with a quantity of ammonia, not sufficient for its complete decomposition, yields slender needles of a *diplumbic salt*, $Pb''S^2O^6.Pb''O$; with an excess of ammonia, a still more basic salt is produced. (Heeren.)

Dithionate of Lithium, $Li^2S^2O^6.2H^2O$, forms indistinct crystals, easily soluble in water, insoluble in alcohol. (Rammelsberg.)

Dithionate of Magnesium, $Mg''S^2O^6.6H^2O$, forms six-sided tables, permanent in the air, and very soluble in water.

Dithionate of Manganese, $Mn''S^2O^6.6H^2O$, prepared as already described (p. 636), crystallises, by spontaneous evaporation, in rose-coloured, mostly indistinct, deliquescent crystals (Marignac). According to Kraut (Jahresb. 1861, p. 118), it forms crystals containing 3 at. water. According to Guthe, these crystals are trimetric, exhibiting the combination $P \,.\, \infty\breve{P}\infty \,.\, \infty\bar{P}2$. Angles P . P in the terminal edges = 90° 32′ and 139° 36′; whence $\infty P : \infty P$ (macr.) = 31° 6′; $\infty\breve{P}2 : \infty\breve{P}2$ (macr.) = 91° 13′.

Dithionates of Mercury.—The mercurous salt, $Hg^2S^2O^6$, separates in colourless indistinct crystals, on evaporating a solution of recently precipitated mercurous oxide in the aqueous acid. It dissolves with difficulty in cold water, and is decomposed by hot water. When heated, it is resolved into mercury, sulphurous oxide, and sulphate of mercury (Rammelsberg).—A *basic mercuric dithionate* appears to be formed by digesting aqueous dithionic acid with excess of mercuric oxide.

Dithionate of Nickel, $Ni''S^2O^6.6H^2O$, separates by spontaneous evaporation in large, thin, green prisms. Its solution mixed with ammonia deposits the ammoniacal salt, $Ni''S^2O^6.6NH^3$, as a blue powder, which crystallises from solution in warm aqueous ammonia, in tabular prisms of a fine violet-blue colour; it is decomposed by water.

Dithionate of Potassium, $K^2S^2O^6$, prepared by decomposing the baric or manganous salt with an exactly equivalent quantity of potassic carbonate (or the baric salt with potassic sulphate), separates on evaporation, in crystals which are permanent in the air, decrepitate when heated, and are resolved at higher temperatures into sulphurous oxide and sulphate of potassium. It dissolves in 16 pts. of cold and 1½ pts. boiling water, but is insoluble in alcohol. (Heeren.)

Dithionate of Rubidium, $Rb^2S^2O^6$, crystallises isomorphously with the potassium-salt, in hard glassy crystals, belonging to the hexagonal system, and exhibiting the combination $\infty P \,.\, \infty P2 \,.\, oP \,.\, P \,.\, 2P2$. Length of principal axis = 0·6307. Angle P : P (terminal) = 145° 46′; P : P (lateral) = 72° 8′. (Piccard, J. pr. Chem. lxxxvi. 449.)

Dithionate of Silver, $Ag^2S^2O^6.2H^2O$.—Prepared by dissolving carbonate of silver in the aqueous acid, and crystallises in right rhombic prisms, permanent in the air (Heeren). By evaporating a solution of the salt mixed with sulphurous acid, at a temperature not exceeding 5°, Kraut obtained it in large crystals containing 6 or 7 at. water. Its solution in warm aqueous ammonia yields small shining crystals of the salt $Ag^2S^2O^6.4NH^3.H^2O$. (Rammelsberg.)

Dithionate of Sodium, $Na^2S^2O^6.2H^2O$, prepared like the potassium-salt, crystallises by spontaneous evaporation, in large, transparent, right rhombic prisms, permanent in the air, having a bitter taste, easily soluble in water, insoluble in alcohol (Heeren). It is optically biaxial and positive, and exhibits considerable dispersion, the angle of the axes being, in the air, for red light, 126° 25′, for violet, 134° 40′.

Dithionate of Sodium and Silver, $AgNaS^2O^6.2H^2O$, is obtained by spontaneous evaporation of a solution containing equivalent proportions of sodic and argentic dithionates, and recrystallisation, in large crystals, apparently isomorphous with its component salts, and exhibiting very distinct cleavage. They effloresce over oil of vitriol, but not in the open air. (Kraut.)

Dithionate of Strontium, $Sr''S^2O^6.H^2O$, prepared like the barium-salt, forms hexagonal crystals, isomorphous with the calcium- and lead-salts, and indistinctly cleavable parallel to oP. The crystals are permanent in the air, easily soluble in water, exhibit negative double refraction, and strong dispersion.

Dithionate of Thallium, $Tl^2S^2O^6$, is very soluble in water, and separates in vitreous tabular crystals, apparently isomorphous with the potassium-salt. (G. Werther, J. pr. Chem. xci. 385.)

The *Dithionates of Yttrium, Erbium*, and *Terbium* are crystallisable.

Dithionate of Zinc, $Zn''S^2O^6.6H^2O$.—This salt is very soluble in water, and its solution rarely yields distinct crystals (Heeren). Its solution in warm, concentrated, aqueous ammonia deposits, on cooling, small prisms of the salt $Zn''S^2O^6.4NH^3$. (Rammelsberg.)

Trithionic Compounds.

TRITHIONIC ACID, $H^2S^3O^6$. *Sulphuretted Hyposulphuric Acid.* (Langlois, Ann. Ch. Phys. [2], lxxix. 77.—Pelouze, *ibid.* lxxix. 85.—Kessler, Pogg. Ann. lxxiv. 250.)—This acid, discovered by Langlois in 1842, is obtained as a potassium-salt:—1. By gently heating an aqueous solution of acid potassic sulphite with sulphur:

$$\underset{\text{Acid sulphite.}}{6KHSO^3} + S^2 = \underset{\text{Trithionate.}}{2K^2S^3O^6} + \underset{\text{Hyposulphite.}}{K^2S^2O^3} + 3H^2O.$$

A saturated solution of the acid sulphite is digested with sulphur for some days at a moderate heat, till the yellow colour at first produced has disappeared. Sulphurous oxide is then evolved, and trithionate of potassium is left in solution, mixed with hyposulphite and sulphate (the latter resulting from the decomposition of the trithionate by heat). The warm filtered solution yields crystals of the trithionate, mixed with sulphur and a small quantity of sulphate: they may be purified by dissolving them in the smallest possible quantity of lukewarm water, and leaving the filtered solution to crystallise by cooling. (Langlois.)

2. By the action of sulphurous acid on hyposulphite of potassium:

$$2K^2S^2O^3 + 3SO^2 = 2K^2S^3O^6 + S.$$

A very concentrated solution of the hyposulphite is prepared by adding it to a mixture of 8 pts. water and 1 pt. alcohol, till the alcohol separates out; and through this solution warmed to 25°—30°, and kept in a state of concentration by frequent addition of the solid salt, sulphurous acid gas is passed, till the liquid turns yellow and smells of sulphurous acid. The liquid then deposits a considerable quantity of crystals of potassic trithionate, after which it becomes colourless, no longer smells of sulphurous acid; and if again saturated with hyposulphite, and treated with sulphurous acid, will yield a fresh quantity of the trithionate. To purify this salt, it is dissolved in water of 60° or 70°; and the solution, freed from sulphur by filtration, is mixed with eight times its volume of alcohol of 84 per cent., then gently warmed, and left to crystallise by cooling (Plessy, Ann. Ch. Phys. [3], xx. 162).—According to Rathke (Jahresb. 1864, p. 164), a mixed solution of hyposulphate and acid sulphite of potassium, yields very pure crystals of the trithionate. Rathke has also observed that the solution which yields these crystals is not precipitated, or but very slightly, by mercuric cyanide at the boiling heat, whereas this salt forms an immediate precipitate in a solution of the crystals themselves, even when very dilute; further, that the original solution, if not too concentrated, does not deposit sulphur on boiling, whereas the solution of the crystals themselves deposits it immediately. Hence Rathke concludes that the trithionate is not contained in the original solution, but is formed only at the moment of crystallisation: this appears also to be the case in the preparation of the salt by Langlois's method.—According to Langlois, a solution of sulphide of potassium may be used in the preceding mode of preparation, instead of the hyposulphite.

3. Chancel and Diacon (Compt. rend. lvi. 720) prepare trithionate of potassium by converting 2 pts. of potassic hydrate into acid sulphite, and 1 pt. into monosulphide; then pouring the former solution, with agitation, into the latter; saturating the mixture with sulphurous acid, evaporating quickly in thin layers, and dissolving the separated salt in water of 60° mixed with a little alcohol. The filtered solution, on cooling, deposits the trithionate in prismatic crystals. Its formation is represented by the equation:

$$4KHSO^3 + K^2S + 4SO^2 = 3K^2S^3O^6 + 2H^2O.$$

Trithionic acid separated from the concentrated solution of its potassium-salt by precipitating the potassium with an equivalent quantity of tartaric, perchloric, or silicofluoric acid, is a limpid inodorous liquid, having a sour and somewhat harsh and bitter taste. It is permanent in the dilute state; but on attempting to concentrate it in a vacuum over oil of vitriol, it begins to decompose, even at 0°, sulphurous oxide being evolved, sulphur deposited, and sulphurous acid remaining in solution: at 80° the decomposition takes place more quickly. By *nitric*, *chloric*, or *iodic acid*, it is immediately converted into sulphuric acid, with separation of sulphur. When boiled with *potash*, it is converted, according to Kessler, into hyposulphite and sulphate of potassium, as shown by the equation:

$$H^2S^3O^6 + 4KHO = K^2S^2O^3 + K^2SO^4 + 3H^2O.$$

According to Fordos and Gélis, the products of the decomposition are hyposulphite and sulphite.

The trithionates $M^2S^3O^6$ and $M''S^3O^6$, are but little known; they appear, however, to be all soluble in water, and are characterised by extreme instability. When heated to redness, or boiled with water, either alone or with addition of the acid, they are converted into sulphates, with evolution of sulphurous oxide and deposition of sulphur. Nitric acid and chlorine-water also quickly convert them into sulphates.

A solution of *silver-nitrate* forms, in a solution of potassic trithionate, a white precipitate, which gradually turns black.—*Mercurous nitrate* immediately forms a black precipitate, which after a while becomes perfectly white, and does not afterwards change colour on boiling. With a small quantity of mercurous nitrate, however, a permanently black precipitate is formed.—*Mercuric chloride* in small quantity produces a black; in excess, a white precipitate.—*Mercuric cyanide* forms no precipitate at first, but after some time a yellow precipitate, which turns black gradually in the cold, immediately on boiling.—*Cupric sulphate* boiled with potassic trithionate produces an immediate separation of sulphide of copper.

Trithionate of Ammonium is produced, together with sulphate, by saturating dry ammonia-gas with dry sulphurous oxide, and dissolving the product in water.

Trithionate of Barium, $Ba''S^3O^6.2H^2O$, is produced (according to Kessler) by saturating the acid with carbonate of barium, and mixing the solution with a large excess of absolute alcohol. The salt then separates in shining laminæ. Its solution decomposes very easily, depositing sulphate of barium.

Trithionate of Potassium, $K^2S^3O^6$, prepared as above described, crystallises in four-sided prisms bevelled with two faces. It has a slightly saline and bitter taste, and is insoluble in alcohol. The aqueous solution is neutral, and is decomposed by heat into sulphur, sulphurous oxide, and sulphate. The dry salt decomposes in like manner at 125°. According to Chancel and Diacon, it is converted by monosulphide of potassium into hyposulphite, without separation of sulphur:

$$K^2S^3O^6 + K^2S = 2K^2S^2O^3.$$

Trithionate of Zinc is produced, with separation of sulphide of zinc, by gradual decomposition of a concentrated solution of the hyposulphite. (Fordos and Gélis.)

Tetrathionic Compounds.

TETRATHIONIC ACID, $H^2S^4O^6$. *Acid hyposulfurique bisulfuré.* (Fordos and Gélis [1843], Ann. Ch. Pharm. xliv. 247.—Kessler, Pogg. Ann. lxxiv. 253.—Chancel and Diacon, Compt. rend. lvi. 510; Jahresb. 1863, p. 150.)—The salts of this acid are produced by the action of iodine on hyposulphites, thus:

$$2Ba''S^2O^3 + I^2 = Ba''I^2 + Ba''S^4O^6.$$

The barium-salt is prepared by adding iodine, in small successive portions, to hyposulphite of barium suspended in a very small quantity of water; after complete saturation, the crystalline pulp is digested with strong alcohol, which dissolves the iodide of barium and excess of iodine, and leaves the tetrathionate in the form of a white powder, which may be purified by dissolving it in the smallest possible quantity of water, and leaving the solution to evaporate. (Fordos.)

A salt of tetrathionic acid is also produced by carefully adding sulphuric acid to a mixture of hyposulphite and peroxide of lead or barium, according to the equation:

$$2PbS^2O^3 + PbO^2 + 2H^2SO^4 = PbS^4O^6 + 2PbSO^4 + 2H^2O;$$

further, by the action of peroxide of lead on pentathionic acid (Chancel and Diacon):

$$4H^2S^5O^6 + 5PbO^2 = 5PbS^4O^6 + 4H^2O.$$

Tetrathionic acid may be prepared by decomposing the barium- or lead-salt with the exact quantity of sulphuric acid required. According to Kessler, the lead-salt is better adapted for the purpose than the barium-salt, because the acid, in presence of strong bases, is apt to decompose, especially at the moment of liberation, into trithionic acid and free sulphur. The lead-salt must be decomposed by sulphuric, not by sulphydric acid, as in the latter case it would be converted partly, or perhaps entirely, into pentathionic acid by the action of the sulphide of lead produced in the reaction.

Tetrathionic acid is a colourless, inodorous, very acid liquid, of about the same degree of stability as dithionic acid. In dilute solution it may be boiled without decomposition, but in the concentrated state it is decomposed by heat into sulphuric acid, sulphurous acid, and sulphur. It is not decomposed by hydrochloric or dilute sulphuric acid in the cold, but a moderately dilute solution, heated with *hydrochloric acid*, gives off sulphuretted hydrogen. When heated with *nitric acid*, it evolves off red fumes, and deposits sulphur.—*Chlorine* converts it into sulphuric acid.

The tetrathionates $M^2S^4O^6$ and $M''S^4O^6$ are all easily soluble in water, but insoluble in alcohol, and are precipitated from their aqueous solutions by alcohol. They are produced either by saturating the acid with bases, or by double decomposition from the lead-salt. The solutions cannot, however, for the most part be evaporated without decomposition, the tetrathionates of the stronger bases being thereby converted into salts of acids containing a smaller proportion of sulphur, and those containing easily reducible bases being resolved into sulphide and sulphate.

Tetrathionic acid and its salts form, with *cupric sulphate*, a brown precipitate after long boiling; with *mercurous nitrate* a yellow precipitate, which slowly blackens on boiling; with *mercuric chloride*, by degrees, a yellowish precipitate, consisting of a compound of chloride and sulphide of mercury mixed with free sulphur; with *mercuric cyanide*, by degrees, a yellow precipitate, which blackens slowly in the cold, immediately on boiling; with *nitrate of silver*, a yellow precipitate, which soon turns black. When tetrathionic acid is supersaturated in the cold with ammonia, no alteration is produced in it by the addition of *ammoniacal solution of silver-nitrate*, or *mercuric cyanide*, or *sulphydric acid* (Kessler). This last reaction distinguishes tetrathionic from pentathionic acid. It is further distinguished from pentathionic acid by not being decomposed by peroxide of lead; and from all the other polythionic acids by the reaction of its potassium-salt with monosulphide of potassium, whereby it is converted into hyposulphite of potassium, with separation of sulphur: $K^2S^4O^6 + K^2S = 2K^2S^2O^3 + S$. (Chancel and Diacon.)

Tetrathionate of Barium, $Ba''S^4O^6.2H^2O$, may be prepared as above described. According to Kessler, it is obtained in large tabular crystals, by mixing the aqueous acid with an equivalent quantity of acetate of barium, and adding absolute alcohol.

Tetrathionate of Cadmium, obtained by double decomposition, separates, on evaporation in a vacuum, as a very deliquescent mass. (Kessler.)

Tetrathionates of Copper.—The *cupric salt* has not been obtained in the solid form. Its solution, when concentrated in a vacuum, deposits a large quantity of brown shining scales, whilst sulphuric acid and cupric sulphate remain in solution.—The *cuprous salt*, $Cu^2S^4O^6$, is produced by the action of hyposulphite of barium on sulphide of copper. It decomposes easily, even at ordinary temperatures, and still more when heated, into cupric sulphide and sulphuric anhydride: $Cu^2S^4O^6 = 2Cu''S + 2SO^3$. (Chancel and Diacon.)

Tetrathionate of Iron (ferrous), $Fe''S^4O^6$, is produced by the action of a ferric salt on ferrous hyposulphite: it is resolved on evaporation into ferrous sulphate, sulphurous acid, and sulphur. (Fordos and Gélis.)

Tetrathionate of Lead, $Pb''S^4O^6.2H^2O$, cannot be crystallised by evaporation, but separates in shining needles, on adding alcohol to the mixed concentrated solutions of plumbic acetate and tetrathionic acid. (Kessler.)

Tetrathionate of Nickel is obtained, as a deliquescent mass, by evaporating its solution in a vacuum.

Tetrathionate of Potassium, $K^2S^4O^6$, is prepared by the gradual addition of iodine to a concentrated solution of potassic hyposulphite, till the reddish-brown colour becomes permanent. The tetrathionate separates completely, and is dissolved in hot water; the solution is then filtered from free sulphur, and mixed with alcohol till the precipitate at first formed slowly redissolves in the liquid. On cooling, the salt separates in large crystals. When tetrathionic acid is added to a concentrated solution of potassic acetate, the salt separates in a pulverulent form, in which state it is more stable than when in large crystals. (Kessler.)

Tetrathionate of Sodium is prepared like the potassium-salt, but requires large quantities of alcohol to precipitate it from its aqueous solution. It melts in its water of crystallisation, when gently heated, with separation of sulphur and evolution of sulphurous oxide. (Kessler.)

Tetrathionate of Strontium, $Sr''S^4O^6.6H^2O$, may be prepared like the barium-salt, but is not so completely precipitated by alcohol. It separates by spontaneous evaporation in thin prisms, but is at the same time decomposed, for the most part, into sulphate of strontium, sulphurous acid, and sulphur. (Kessler.)

Pentathionic Compounds.

PENTATHIONIC ACID, $H^2S^5O^6$. (Wackenroder [1845], Ann. Ch. Pharm. lx. 189.—Lenoir, *ibid.* lxii. 253.—Fordos and Gélis, Ann. Ch. Phys. [3], xxii. 66.—Kessler, Pogg. Ann. lxxiv. 257.—Ludwig, Arch. Pharm. [2], lxxxv. 9.—Chancel and Diacon, Compt. rend. lvi. 710.)—This acid is produced by the mutual action of sulphurous and sulphydric acids:

$$5H^2SO^3 + 5H^2S = H^2S^5O^6 + 9H^2O + S^5.$$

To prepare it, Wackenroder passes sulphydric acid gas in excess through a saturated aqueous solution of sulphurous acid, filters, and digests the milky filtrate with slips of clean metallic copper, till it becomes clear—filters again—removes the dissolved copper by sulphydric acid, and drives off the excess of the latter by a gentle heat. The solution thus obtained is colourless, and destitute of odour; it may be concentrated, without decomposition, till it attains the specific gravity of 1·37.—Kessler passes sulphurous and sulphydric acid gases alternately through water, till the precipitated sulphur forms a thick magma at the bottom of the vessel; digests the filtered liquid with freshly precipitated carbonate of barium, to remove sulphuric acid; filters, and concentrates the filtrate over a water-bath, till it attains a density of 1·25—1·3. The acid liquid thus obtained may be further concentrated, in a vacuum, to the density of 1·6 at 22°.

According to Risler-Bonnet (Pogg. Ann. cxvi. 470; Jahresb. 1861, p. 60), pentathionic acid is also produced by the reaction of zinc on sulphurous acid; the zinc first dissolves in the acid, with evolution of hydrogen, which at the moment of liberation decomposes part of the sulphurous acid, yielding water and sulphydric acid; and the latter reacts on the sulphurous acid, so as to form pentathionic acid:

$$10H^2SO^3 + 5H^2S = 3H^2S^5O^6 + 12H^2O.$$

The solution exhibits the reactions of pentathionic acid as long as it retains free sulphurous acid, but the pentathionic acid is subsequently resolved into sulphuric acid, hyposulphurous acid, and free sulphur.

Pentathionic acid is colourless and inodorous, and has a strongly acid taste, inclining to bitter. It may be preserved unchanged at the temperature of the air; but on attempting to concentrate it, by heating beyond the density of 1·37, it is decomposed, sulphydric acid and afterwards sulphurous acid being evolved, while sulphuric acid and sulphur remain behind. It is not decomposed by sulphydric acid, or by dilute hydrochloric or sulphuric acid; the latter, however, when concentrated, decomposes it. By nitric acid, hypochlorous acid, or chlorine, it is oxidised, and converted into sulphuric acid. Metallic copper and iron decompose it at the boiling heat, the former with evolution of sulphurous acid and formation of sulphide of copper; the latter with evolution, first of sulphydric acid, then of sulphurous acid, a portion of the latter also remaining in the liquid (Wackenroder). A moderately concentrated solution of pentathionic acid gives off a faint sulphurous smell when boiled, but does not evolve sulphurous acid gas except when highly concentrated; on boiling it with hydrochloric acid, the odour of sulphydric acid is perceptible. On boiling the acid with solution of caustic potash, hyposulphite, sulphate, and sulphide of potassium are formed. (Kessler.)

The reactions of pentathionic acid with *cupric sulphate, mercurous nitrate, mercuric chloride, mercuric cyanide,* and *nitrate of silver,* are the same as those of tetrathionic acid. With *ammoniacal nitrate of silver,* however, it reacts differently.

When a solution of pentathionic acid is rapidly mixed with excess of ammonia, the addition of an ammoniacal solution of silver-nitrate quickly produces a brown colour, which gradually becomes darker, while sulphide of silver separates from the liquid (Kessler). According to Risler-Bonnet, it produces an immediate black precipitate. An ammoniacal solution of *mercuric chloride* added to the same liquid gradually produces a black precipitate of sulphide of mercury; and on the addition of sulphydric acid, a separation of sulphur takes place (Kessler). A recently prepared solution of pentathionic acid mixed with potash, decolorises a solution of indigo. (Risler-Bonnet.)

The pentathionates have not been much examined. They are very unstable, so much so, that it is difficult to obtain them in the solid state. In fact, the fifth atom of sulphur in the acid appears to be retained by only a feeble affinity; and in presence of a strong base, especially if the solution be concentrated, this last atom of sulphur is separated, and the pentathionic acid is reduced to tetrathionic acid, the salts of which have greater stability. Sometimes two atoms of sulphur are given up, and trithionic acid is produced. Kessler found that on mixing a solution of pentathionic acid of specific gravity 1·32, with alcohol of 96 per cent., washing the precipitate with alcohol, and dissolving it in warm water, a considerable quantity of sulphur remained undissolved; and the solution mixed with alcohol yielded crystals, having the form and composition of potassic tetrathionate.

The pentathionates of barium and lead are soluble in water, but cannot be obtained in the solid state by evaporation, even in a vacuum, decomposition taking place as soon as the solutions attain a certain degree of concentration. Lenoir, however, obtained the barium-salt, $Ba''S^5O^6.H^2O$, in definite crystals, by mixing the freshly prepared aqueous solution with strong alcohol. The salt then separated abundantly in transparent silky prisms, which changed within the liquid to larger and well-defined crystals.

Pentathionate of Potassium, $K^2S^5O^6$, crystallises (according to Rammelsberg, Jahresb. 1857, p. 136) in monoclinic prisms, exhibiting the combination $\infty P . [\infty P3] . \infty P\infty . +P . -P . +P3 . -P3$. Axes $a : b : c = 1 : 0·9285 : 1·2639$. Angle $b : c = 78° 45'$; $\infty P : \infty P$ (clinod.) $= 95° 24'$; $+P : +P$ (clinod.) $= 101° 38'$; $-P : -P$ (clinod.) $= 112° 12'$.

SULPHUR-ACIDS, or **SULPHANHYDRIDES.** Names sometimes applied to the sulphides of the more electronegative metals (arsenic, antimony, &c.), which, in combination with the electropositive sulphides, form sulphur-salts.

SULPHUR-BASES. The sulphides of the more electropositive metals, potassium, barium, copper, lead, &c.

SULPHURET. Syn. with Sulphide (p. 482).

SULPHURIC ACID and **ANHYDRIDE.** See Sulphur, Oxides and Oxygen-acids of (p. 569).

SULPHURIC CHLORIDE (p. 576).

SULPHURIC ETHERS (p. 620).

SULPHUROUS ACID and **ANHYDRIDE.** See Sulphur, Oxides and Oxygen-acids of (p. 540).

SULPHUROUS CHLORIDE (p. 542).

SULPHUROUS ETHERS (p. 551).

SULPHUR-SALTS. Compounds analogous to oxygen-salts, composed of sulphur-acids or sulphanhydrides and sulphur-bases: *e.g., sulpharsenate of potassium,* K^3AsS^4, or $3K^2S.AsS^5$, &c.

SULPHURYL, SO^2. The radicle of sulphuric acid and its derivatives.

SULZBERITE. Syn. with strontianite, or native carbonate of strontium. (See CARBONATES, i. 797.)

SUMACH. The powder of the dried leaves of various shrubs and trees of the genus *Rhus* (order *Terebinthaceæ*), especially of *Rh. coriaria* and *Rh. cotinus*. It contains colouring-matter and tannin, and is used in dyeing and calico-printing, as a substitute for nut-galls, in the production of grey colours, and in Turkey-red dyeing; also for tanning the finer kinds of leather. According to Chevreul, it contains a yellow colouring-matter, which separates from a concentrated decoction on cooling, in small crystalline grains. It forms a yellow precipitate with solution of alum, and may, therefore, be used for communicating a yellow dye to stuffs mordanted with alum. The decoction of sumach reacts strongly acid with litmus, gives a yellowish-white precipitate with stannous chloride, pale-yellow with acetate of lead, yellowish-brown with cupric acetate, and a blue flocculent precipitate with ferric chloride.

SUMBULAMIC ACID. A peculiar acid, contained (according to Reinsch) together with angelic acid, in sumbul-root.

SUMBUL-BALSAM. See SUMBUL-ROOT.

SUMBULIC ACID. The name given by Reinsch to an acid contained in sumbul-root, which he at first regarded as distinct from angelic acid, because its alcoholic solution is coloured blue by sulphuric acid; but, according to later experiments by Rieckher and Reinsch (Jahrb. pr. Pharm. xvi. 12), it does not exhibit this coloration when quite pure and free from sumbulamic acid, and must therefore be regarded as identical with angelic acid, with which it agrees in all other respects.

SUMBULINE. The name given by Murawieff to an alkaloïd supposed to exist in sumbul-root.

SUMBUL-OIL. A mixture of volatile oils obtained by the distillation of sumbul-balsam.

SUMBULOLIC ACID. Syn. with SUMBULIC or ANGELIC ACID.

SUMBUL-ROOT. *Musk-root.* The root of an umbelliferous plant, said to be indigenous in Persia. It usually occurs in commerce, in rather large cakes having a strong musk-like odour, and a faintly sweetish musklike taste, with aromatic burning aftertaste, like angelica and imperatoria root. Reinsch found in 100 pts. of sumbul-root 13 pts. water, 12·9 balsam, 28·4 starch and salts, 8 gum, 4 colouring-matter soluble in alcohol, 7 bitter substance, and 5 ash-constituents (containing a large quantity of potassic carbonate), besides mucilage, woody fibre, resin, wax, and traces of volatile oil not smelling of musk.

According to Reinsch, the balsam extracted from the root by ether has the colour and consistence of copaiba-balsam, a burning taste, and only a faint musk-like odour in the dry state, but gives out a strong odour of musk when in contact with water. Strong sulphuric acid dissolves it with fine blue colour. By dry distillation, the balsam gives off—first, a yellowish oil tasting like peppermint; afterwards a grass-green oil having the odour of cajeput, while the residue acquires an indigo-blue colour. On continuing the distillation, a blue oil passes over, which dissolves with blue colour in alcohol; paper on which the solution is dropt, acquires a musklike odour after a few days. The oil is coloured green by cold potash-ley; hot potash-ley dissolves it. The balsam dissolves in potash-ley, and, on adding water, a resinous mass separates, containing the potassium-salt of sumbulamic acid, which may be separated from it by dilute sulphuric acid. This acid is resinous at first, but is converted into a crystalline mass by long contact with water; it is said to form an ether. Further investigation is required to determine how far this acid differs from sumbulic or angelic acid.

Sommer (Arch. Pharm. cxxxviii. 1) has also investigated sumbul-root, but with somewhat different results. The extract obtained from the root by treatment with ether, gave, by distillation with water, a very small quantity of a pale-yellow, neutral, volatile oil, which in the concentrated state smelt more like angelica-root, but in the dilute state more like musk. This oil is mobile and lighter than water, but resinises quickly in contact with the air, becoming viscid, darker-coloured, and acid. It dissolves in nitric acid with violet colour, soon changing to yellow; by sulphuric acid it is turned brown, and carbonised. The balsam prepared with ether or alcohol yields by dry distillation (according to Sommer) one-third of its weight of a greenish mobile oil, smelling like creasote; afterwards white fumes are evolved, which thicken to a blue oil (about one-third of the resin); finally, tarry products pass over, and a carbonaceous residue is left. The blue oil sometimes contains needle-shaped crystals, which likewise condense in the neck of the retort.

The blue oil is a mixture of several bodies; it begins to boil at 150°, a pale-yellow oil then passing over; at 200°—280°, a light-blue, and at 285°—325° a dark-blue oil passes over, at which latter temperature partial decomposition takes place. The blue oil has a peculiar, not very agreeable odour, is lighter than water, slightly soluble therein, easily soluble in alcohol and ether. Heated with nitric acid, it yields oxalic acid. When distilled with potash, it gives off a neutral pale-blue oil, smelling like bergamot pears; and the residue, treated with sulphuric acid, gives off the odour of valerianic acid. The crystals obtained, together with the blue oil, consist of umbelliferone (*q. v.*). (Sommer.)

Sumbul-root is said to cause trembling and weakness of the limbs, confusion of the head, acceleration of the pulse, increased heat, and greater activity of the stomach. (Handw. d. Chem. viii. 440.)

SUNDVIKITE. A mineral from Kimito in Finland, allied to, and perhaps identical with, anorthite. (*Rammelsberg's Mineralchemie*, p. 593.)

SUNSTONE. Oligoclase from Tvedestrand in Norway (iv. 198).

SUPER. A prefix synonymous with PER (iv. 374).

SUPERPHOSPHATE. Acid phosphate of calcium, prepared on the large scale for manure, by treating bones, coprolites, &c. with sulphuric acid.

SURINAMINE. An alkaloïd, occurring, according to Hüttenschmidt (Mag. Pharm. vii. 287), in the bark of *Geoffroya inermis*.

SURTURBRAND. Fibrous lignite, so called in Iceland, where it occurs in large quantities.

SUSANNITE, or **SUZANNITE.** A sulphato-carbonate of lead having the same composition as leadhillite (27·5 per cent. $PbSO^4$ and 72·5 $PbCO^3$), but crystallising in rhombohedral forms, derived from a primitive rhombohedron in which the length of the principal axis is 1·1062 and R : R = 94°; it exhibits the faces −2R, ∞R, oR, and cleaves easily parallel to oR. Hardness = 2·5. Specific gravity = 6·55. Lustre resinous to adamantine. Colour white, green, yellow, and brownish-black. Streak uncoloured. It occurs in attached crystals at Leadhills in Scotland, and at Moldawa in the Bannat. (Dana, ii. 373.)

SVANBERGITE. A mineral discovered by Ijelström (Jahresb. 1854, p. 681), together with lazulite, on the Horrsjöberg in Wermland, Sweden, in cube-like rhombohedrons, resembling those of beudantite, and cleaving parallel to the terminal face. Hardness = 5·0. Specific gravity = 3·30. Colour pale red, or yellow. Transparent to translucent. Before the blowpipe it becomes decolorised, and melts only in thin splinters. The pulverised mineral dissolves partially in strong acids, and the residue becomes incandescent when heated. Contains 17·32 per cent. SO^3, 17·8 P^2O^5, 37·84 Al^2O^3, 1·40 FeO, 6·0 lime, 12·84 Na^2O, and 6·80 water, with a trace of chlorine; whence the formula is, perhaps, $2(2Al'''HO^2.Na^2SO^4) + (2Al'''HO^2.Ca''P^2O^6)$, or, according to Rammelsberg (*Mineralchemie*, p. 361), $(\frac{2}{3}Na^2O.\frac{1}{3}CaO)^3.P^2O^5 + (3Al^2O^3.2SO^4) + 3H^2O$.

SWAGA. The Thibetian name for borax.

SWAMP-ORE. Bog iron-ore.

SWIETENIA. A genus of trees belonging to the meliaceous order. The bark of *Swietenia senegalensis*, or *Cail-cedra*, is used in Senegal as a febrifuge. The bark of *Sw. febrifuga*, indigenous in India, is the *Cortex Soyamidæ*, which, according to Duneau (Trommsdorff's Journal, iii. 257), contains a bitter principle, tannin, volatile oil, and resin. According to Overbeck (Arch. Pharm. [2] lxviii. 271), the bark contains an amorphous bitter principle, but no base.

SYCOCERYLIC ACID. See the next article.

SYCOCERYLIC ALCOHOL. $C^{18}H^{30}O = \left.\begin{matrix}C^{18}H^{29}\\H\end{matrix}\right\}O$. (De la Rue and Müller, Phil. Trans. 1860, p. 43; Chem. Soc. Qu. J. v. 62.)—This compound, homologous with benzylic alcohol (C^7H^8O) and cymylic alcohol ($C^{10}H^{14}O$), is produced by treating sycocerylic acetate (*infra*) with sodium-alcohol, and purified by precipitation with water and crystallisation from ordinary alcohol. It forms very thin crystals, resembling caffeine, usually aggregated in masses like wavellite; melts at 90° to a liquid heavier than water, and solidifies in the crystalline state on cooling; after being strongly heated, it solidifies to a transparent glass, which becomes crystalline in contact with alcohol; distils partly undecomposed.—It is insoluble in *water*, aqueous *ammonia*, and *alkalis*

It dissolves readily in *ethylic alcohol*: a hot saturated solution forms a semisolid mass of crystals on cooling; a solution in very dilute alcohol deposits, on cooling, a jelly, which afterwards becomes crystalline. Dissolves in *ether*, *benzene*, *chloroform*, and *light mineral oil*.

Decompositions.—1. Sycocerylic alcohol is but slowly attacked by boiling with dilute *nitric acid*: the dark-yellow resin formed after six hours, when washed and dried, and afterwards dissolved in warm alcohol, yields white and yellow crystals, easily soluble in aqueous ammonia and potash, and precipitable by alcoholic neutral acetate of lead; probably a mixture of sycocerylic acid, $C^{18}H^{28}O^{2}$, and nitrosycocerylic acid.—2. Moderately dilute aqueous *chromic acid*, boiled with sycocerylic alcohol for eight hours, produces no sycocerylic acid: on one occasion, neutral thin prisms, probably of sycocerylic aldehyde, $C^{18}H^{28}O$, were produced.—3. The alcohol dissolves easily in *oil of vitriol*, forming a brown solution, from which water throws down a viscid resin; no conjugated compound of sulphuric acid remains in solution.—4. Sycocerylic alcohol is readily attacked by *chlorine* and *bromine*, and forms yellow crystals with *iodine*.—5. A solution of sycocerylic alcohol in benzene evolves hydrochloric acid gas when treated with *pentachloride of phosphorus* at 60°. If, after the evolution of gas has ceased, the remaining chloride of phosphorus be removed, and the benzene solution washed with water and aqueous alkali and evaporated, there remains an amorphous, greenish, viscid residue, easily soluble in ether and chloroform, but difficultly soluble in alcohol. On one occasion crystals were also obtained.—6. *Potassium* evolves hydrogen from melted sycocerylic alcohol, and becomes covered with a white crust, which, when heated till it melts, blackens and takes fire.—7. Sycocerylic alcohol, treated with fused *caustic potash*, evolves hydrogen without forming sycocerylic acid. —8. With *chloride of acetyl* it forms acetate of sycoceryl, and with *chloride of benzoyl* benzoate of sycoceryl.

SYCOCERYLIC ALDEHYDE. See the last article.

SYCOCERYLIC ETHERS. (De la Rue and Müller, *loc. cit.*) ***Sycocerylic Acetate***, $C^{20}H^{32}O^{2} = C^{2}H^{3}(C^{18}H^{29})O^{2}$.—This ether is contained, together with sycoretin, in the resin of *Ficus rubiginosa* from New South Wales (ii. 646). To obtain it, the sycoretin is dissolved out of the resin by cold alcohol, and the residue is boiled with alcohol. The solution, on cooling, deposits crystals of sycocerylic acetate, mixed, towards the end of the crystallisation, with a small quantity of a flocculent substance; and by leaving the solution to cool to 40°, then straining off the liquid, recrystallising the solid residue from boiling alcohol, and treating the product at 30° with a quantity of ether not sufficient to dissolve it, the sycocerylic acetate is obtained pure, while a neutral crystalline substance remains undissolved. Sycocerylic acetate is also produced by treating sycocerylic alcohol with chloride of acetyl.

Sycocerylic acetate crystallises from alcohol, in thin laminæ resembling cholesterin, and from ether in flat six-sided tables. It melts at 118°—120°, and solidifies below 80° to a mass which is transparent at first, but afterwards becomes opaque and crystalline. It distils unchanged; but when it is too strongly heated, the distillate smells rancid, and like acetic acid. It is brittle; strongly electric when rubbed; neutral. It dissolves very easily in hot *alcohol*, and in *acetic acid*, *acetone*, *chloroform*, *ether*, *benzene*, and *oil of turpentine*. It is not precipitated by alcoholic *neutral acetate of lead*, or by aloholic *acetate of copper*.

Hot dilute *nitric acid* converts sycocerylic acetate into a resin. The easily prepared solution in fuming nitric acid is precipitated by water in amorphous yellow flocks. It dissolves easily and without coloration in *oil of vitriol*; the solution becomes brown on standing, and gives off traces of sulphurous and acetic acids; water precipitates from the solution a hard substance, fusible below 100°, difficultly soluble in alcohol, and easily soluble in chloroform and benzene. It forms resinous compounds with *chlorine*, *bromine*, and *iodine*; the last two, when added gradually to a warm alcoholic solution of the acetate, form crystals of a colourless bromine- or iodine-compound, which are deposited on cooling. It is not affected by boiling solution of *caustic potash*, but is decomposed by the fused hydrate, with liberation of hydrogen.—*Sodium-alcohol* decomposes it even at 90°, forming acetic acid and sycocerylic alcohol.

Sycocerylic Benzoate, $C^{25}H^{34}O^{2} = C^{7}H^{5}(C^{18}H^{29})O^{2}$.—Prepared by dissolving sycocerylic alcohol in chloride of benzoyl (no gas being evolved in the cold), and heating the solution as long as hydrochloric acid gas is given off. The crystalline mass formed on cooling is thrown into a warm aqueous solution of acid potassic carbonate, with which it is warmed for several hours. The resin thereby separated, after washing with warm water and boiling alcohol, is dissolved in boiling ether, from which it is obtained in crystals. Boiling absolute *alcohol* dissolves only a trace of the crystalline substance, and deposits it again, on cooling, in small crystals recognisable under the microscope. It dissolves with difficulty in cold *ether*, and in all proportions in *chloro-*

form and *benzene*, crystallising in prisms on evaporation. *Sodium-alcohol* decomposes it only on long boiling, with formation of sycocerylic alcohol and sodic benzoate.

SYCORETIN. The resin of *Ficus rubiginosa* is resolved, by treatment with alcohol, into about 73 per cent. of sycoretin soluble in cold alcohol, 14 per cent. of sycocerylic acetate soluble in hot alcohol, and 13 per cent. of residue, consisting of caoutchouc, sand, and fragments of bark.

On mixing the neutral pale-brown solution in cold alcohol with water, the sycoretin is precipitated, and may be rendered colourless by repeated solution and precipitation. A saturated alcoholic solution deposits, in the cold, a small quantity of a crystalline substance, sycoretin in a purer state remaining in solution. The latter may be separated, by fractional precipitation with water, into two portions, the first of which contains 74·65 per cent. C and 10·11 H; the second, 77·89 per cent. C and 9·94 H.

Sycoretin is amorphous, white, neutral, very brittle, and highly electric. It melts in boiling water to a thick liquid, which floats on the surface. Melts below 100°. Sycoretin is insoluble in *water*, dilute *acids*, *ammonia*, and aqueous *alkalis*. It is not precipitated from its alcoholic solution by *neutral acetate of lead*, or *acetate of copper*.—Dissolves easily in *alcohol*, *ether*, *chloroform*, and *oil of turpentine*. (De la Rue and Müller, *loc. cit.*)

Sycoretin undergoes decomposition at a few degrees above its melting-point, frothing up, and giving off water with a wax-like odour. When further heated, it melts quietly, and yields a distillate containing acetic acid and tar, charcoal being left behind.—It is attacked by *nitric acid*, and dissolved on boiling therewith; water precipitates from the yellow solution a slightly acid nitro-compound, which dissolves with dark colour in aqueous alkalis, and forms an explosive compound with potash. In this reaction a little oxalic acid is formed, but no picric acid.—Sycoretin dissolves in *oil of vitriol* with fine green colour, without forming sugar: water throws down from the solution a brown precipitate, less soluble than sycoretin.—*Caustic potash* acts on sycoretin in the same way as oil of vitriol.

SYENITE. A rock allied to granite, and consisting essentially of a crystallo-granular mixture of orthoclase and hornblende, the former being often more or less replaced by oligoclase. Quartz and mica also occur in syenite, giving it more or less of a granitic character, while, on the other hand, the occurrence of hornblende in granite renders it more or less syenitic; in fact, the two rocks pass into one another by insensible gradations. In like manner the occurrence of rather large crystals or masses of orthoclase in syenite gives rise to transitions between that rock and porphyry; and in other cases, the alternation of layers of hornblende with felspar produces syenitic slate, or (if mica is also present) syenitic gneiss. Titanitic syenite and zircon-syenite are syenites in which titanite and zircon occur imbedded.

SYEPOORITE. Native protosulphide of cobalt, $Co''S$, occurring at Syepoor, in North-western India, in steel-grey crystalline grains or masses, of specific gravity 5·45 (i. 1050).

SYHEDRITE. A silicate, occurring in the trap of Thore-gate, in the Syhedree Mountains, Bombay, in irregularly laminated masses, having a fine-green colour, vitreous lustre, hardness = 3·5, and specific gravity = 2·321. It gives by analysis 56·92 per cent. SiO^2, 15·06 Al^2O^3, 2·71 FeO, 6·45 CaO, 2·4 MgO, and 16·40 water, and therefore approaches in composition to stilbite (p. 433); but it differs from that mineral in colour, and in being less easily decomposed by acids. (Shepard and Tyler, Sill. Am. J. [2] xl. 110; Jahresb. 1865, p. 891.)

SYLVAN. Native tellurium.

SYLVANITE. *Graphic Tellurium. Graphic Gold. Yellow Tellurium. Müllerite. Aurotellurite. Schrifterz. Schrifttellur. Tellure natif auro-argentifère. Aurum graphicum.*—A telluride of gold and silver, sometimes also containing lead and antimony, occurring in narrow veins in the porphyry mountains of Offenbanya and Nagyag, in Transylvania. It contains a large proportion of gold, and is a valuable ore. It forms trimetric crystals, mostly small and needle-shaped, and grouped in such a manner that the combinations are difficult to make out. The crystals frequently also cross one another at angles of 60° and 120°, probably in consequence of twin-formation; and by a repetition of this grouping on the surfaces of rocks, triangular and rhombic figures are produced, like oriental writing characters: hence the name, *graphic tellurium*. The primary form of the crystals is a rhombic prism having the angle $\infty P : \infty P = 110° 48'$; $oP : P\infty = 119° 26\frac{1}{2}'$; and therefore $a : b : c : = 1 : 1·4496 : 1·7721$. The prism ∞P is combined with $\infty\breve{P}2$, $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, oP, forming elongated prismatic crystals, the ends of which are modified by several pyramids and domes. Cleavage very distinct parallel to $\infty\bar{P}\infty$, less distinct parallel to $\infty\breve{P}\infty$. The mineral occurs also imbedded in laminæ and masses.

Hardness = 1·5 to 2. Specific gravity = 7·99 to 8·33. Lustre metallic. Streak and colour pure steel-grey to silver-white, sometimes nearly brass-yellow. Fracture uneven. Very sectile. Before the blowpipe, it melts easily, tinging the flame greenish-blue, covering the charcoal with a white oxide, and finally leaving a ductile metallic globule. It dissolves easily in nitric acid.

The following analyses are by Petz (Pogg. Ann. lvii, 472):—*a.* Thin needle-shaped crystals: specific gravity = 8·28.—*b.* Indistinct crystals: specific gravity = 8·28.—*c.* Long white crystals: specific gravity = 8·27.—*d.* Thick white crystals: specific gravity = 7·99.—*e.* Short yellowish crystals: specific gravity = 8·33.—*f, g.* Light yellow masses:

	Offenbanya.		Nagyag.				
	a	*b.*	*c*	*d.*	*e.*	*f.*	*g.*
Tellurium	59·97	58·81	55·39	48·40	51·52	44·54	49·96
Antimony	0·58	0·66	2·50	8·42	5·75	8·54	3·82
Gold	26·97	26·47	24·89	28·98	27·10	25·31	29·62
Silver	11·47	11·31	14·68	10·69	7·47	10·40	2·78
Lead	0·25	2·75	2·54	3·51	8·16	11·21	13·82
Copper	0·76						
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

These analyses are most easily reduced to a formula on the hypothesis that the tellurium and antimony on the one hand, and the gold, silver, and lead on the other, replace one another isomorphously. On this supposition the whole of the analyses may be included under the general formula $(Au^2; Ag^2; Pb'')(Te; Sb)^3$. The composition of the mineral from Offenbanya is very nearly expressed by the simpler formula, $Au^2Ag^2Te^6$, or $Au^2Te^3.Ag^2Te^3$. This variety is sometimes specially distinguished as graphic tellurium; and that which contains lead and antimony in addition, as white tellurium.

SYLVIC ACID, $C^{20}H^{30}O^2$. (Unverdorben, Pogg. Ann. vii. 311; viii. 40, 407; xi. 28, 230, 393; xiv. 116; xvii. 186.—Trommsdorff, Ann. Ch. Pharm. xiii. 169. —H. Rose, Pogg. Ann. xxxiii. 42; liii. 374.—Laurent, Ann. Ch. Phys. [2], lxv. 324; lxviii. 395; lxxii. 459; [3], xxii. 459.—Sievert, Zeitschr. f. die ges. Naturwissenschaften, xiv. 311; Jahresb. 1859, p. 508.—Maly, Wien. Akad. Ber. xliv. 121; Jahresb. 1861. p. 389.)—This acid was discovered and investigated by Unverdorben, but confounded by him and all later investigators (except Maly), with abietic acid, the acid existing ready-formed in pine-resin. Owing to this confusion, it is not always clear which statements refer to abietic and which to sylvic acid. Unverdorben, however, seems to have examined principally an acid prepared with sulphuric acid—therefore sylvic acid. Laurent's statements apply better to sylvic acid, though his method of preparation must have yielded abietic acid.

Two acids found by Baup (Ann. Ch. Phys. [2] xxxi. 108) in French colophony, *Acide pinique* and *Acide abiétique*, as well as Lecanu and Bussy's *crystallised acid from turpentine* (J. Pharm. xiii. 62), appear also to belong to this head.

Formation and Preparation.—1. *From Abietic Acid.* An alcoholic solution of abietic acid is precipitated by dilute sulphuric acid, and the hardened crystalline precipitate is washed with alcohol, and afterwards crystallised from that liquid (Maly).—Sylvic acid is obtained also, together with sylvinolic acid, by passing hydrochloric acid gas into a solution of abietic acid in alcohol. (Maly.)

2. *From White Pitch, Colophony, &c.*—White pitch is allowed to stand, covered with an equal quantity of alcohol, till it is completely saturated with the liquid, and until the turpentine-like deposit formed at first has become crystalline. It is then collected on a cloth, triturated with a little alcohol, washed with that liquid on the filter, and afterwards dissolved in a small quantity of hot absolute alcohol containing sulphuric acid: the solution, on cooling, solidifies to a crystalline mass. Purification is effected by pressing the crystals, and repeatedly subjecting a hot alcoholic solution to fractional precipitation with hot water, whereby the less pure portions are thrown down first. The alcoholic solution mixed with a quantity of hot water barely sufficient to produce turbidity, yields large crystals on cooling. (Trommsdorff.)

Laurent boils pine-resin with water to free it from turpentine; extracts the pinic acid by means of cold alcohol, and dissolves the residue in boiling alcohol. On cooling, the solution yields crystals, which are freed from adhering oil by washing with cold alcohol, and recrystallisation from boiling alcohol. Unverdorben, and likewise Trommsdorff and Sievert, employ similar methods. The product thus obtained is abietic acid. (Maly.)

Long standing of the alcoholic solution reduces the yield of the crystals. (Sievert.)

Properties.—Sylvic acid forms colourless, transparent, tabular, rhomboïdal prisms, with four-sided summits (Unverdorben); indistinctly crystalline masses, also triangular laminæ (Rose; Laurent). According to Sievert, the crystals are combinations derived from a rhombic prism of 96° and 84°, having the acute lateral edges much truncated, and terminated by sphenoïdal faces, developed to such an extent as completely to obliterate two faces of the prism. They are vitreous, brittle, and triturable to a white powder.

Sylvic acid does not lose weight at 100°, or in a vacuum, and melts without loss of weight (Unverdorben) at 152·5°, but becomes quite fluid at higher temperatures (Trommsdorff). In a warm tube the crystallised acid, as well as that which has been previously fused, melts at 162°; but when heated in a retort, it cakes together (partially at 118°, and completely at 150°), and melts to a thin clear liquid, which turns thick at 120°, viscid at 110°; and solidifies to a glassy mass, afterwards melting partially at 135°, and completely at 155° (Sievert). Sylvic acid sublimes partially at 170°, in a thin crust, which, when dissolved in alcohol, yields crystals of the unchanged acid; the residue turns dark-red at 240°, but does not boil even at 290° (Sievert). It distils without much decomposition, yielding a trace of water, and a colophony-like distillate, an alcoholic solution of which deposits crystals of unchanged sylvic acid, whilst the residue contains a trace of charcoal (Laurent). Inodorous and tasteless; reddens litmus. Rotates a ray of polarised light to the left, more powerfully than pimaric acid. Specific gravity = 1·1011 at 18°. (Sievert.)

Sylvic acid is soluble in *acetic acid.* It dissolves very slightly in cold alcohol of 65 per cent., and in about 3 pts. of the boiling liquid, from which it crystallises on cooling, about $\frac{1}{25}$th only remaining in solution; in about 3 pts. of cold and 1 pt. of boiling absolute alcohol or ether, and is thrown down from the former solution by an equal quantity of water, as a semitransparent oil, which hardens to a crystalline solid on addition of more water, or on exposure to the air (Unverdorben). Sylvic acid is soluble in 10 pts. of cold and in $\frac{4}{5}$ths of boiling alcohol of 92 per cent.; more freely, therefore, than pimaric acid (Sievert). It dissolves in *acetic ether, rock-oil,* and *oil of turpentine,* without crystallising therefrom. (Unverdorben.)

Decompositions.—1. Sylvic acid submitted to *dry distillation* (*supra*) yields water and empyreumatic oil, then a little gas, followed first by a thinner and afterwards by a thicker oil, containing sylvic and pinic acids and a large quantity of a neutral resin and oils.—2. *Nitric acid* slowly decomposes sylvic acid, and dissolves it only on prolonged boiling; water throws down from the solution yellow flocks, soluble in ammonia, caustic potash, and alcohol.—3. *Oil of vitriol* rapidly dissolves sylvic acid, forming a yellowish-brown solution, from which water precipitates unchanged sylvic acid and a large quantity of pinic acid. (Unverdorben.)

Sylvates.—Sylvic acid combines with *bases,* with elimination of water (Unverdorben; Laurent)—(contrary to Rose's statement). It expels the acid from carbonates, and when melted also from succinates and benzoates, and from chloride of calcium; but salts of sylvic acid dissolved in water are decomposed by boric and acetic, and by stronger acids, with precipitation of sylvic acid. The salts are obtained:—α. By dissolving the acid in the aqueous base.—β. By precipitating an acetate dissolved in alcohol by means of alcoholic sylvic acid, dissolving the precipitate in ether, and reprecipitating by alcohol, which retains in solution the excess of sylvic acid.—γ. By double decomposition. Some of the sylvates are crystallisable; a few of them are soluble in water and alcohol, and all of them in ether. (Unverdorben.)

Sylvate of Ammonium is a viscid mass, more soluble in alcohol or ether than in water; decomposed by heat.—The *barium-salt* is precipitated from aqueous solution in crystalline flocks, soluble in 3,000 pts. of water, in 6 pts. of cold and a smaller quantity of boiling absolute alcohol, from which it is deposited in microscopic crystalline flocks on cooling (Unverdorben).—The *normal calcium-salt,* $C^{40}H^{58}Ca''O^4$, is obtained by precipitating the potassium-salt with chloride of calcium, and a salt containing a smaller proportion of calcium is formed by precipitating alcoholic sylvic acid with an alcoholic solution of calcic acetate. (Sievert.)

The *cupric salt,* $C^{40}H^{58}Cu''O^4$, is obtained, in pale-blue flocks, on mixing the alcoholic solutions of sylvic acid and cupric acetate. By dissolving this precipitate in aqueous ammonia, and leaving the solution to cool, or diluting it with water, the same salt is thrown down as a dark-blue mass, triturable to a pale-blue powder when dry. (Sievert.)

The *ferrous* and *ferric salts* dissolve slightly in cold alcohol, easily in ether.

Lead-salt.—The precipitate thrown down by alcoholic sylvic acid from alcoholic plumbic acetate, is a white, amorphous, easily fusible powder, containing, on the average, 26·94 per cent. oxide of lead, agreeing nearly with the formula $C^{40}H^{58}Pb''O^4$, which requires 26·17 PbO (Rose). Sylvic acid heated to 168° with oxide of lead, loses

3·02 per cent. water; calculation from the same formula requires 2·97 per cent. (Sievert.)

The *magnesium-salt* dissolves in all proportions of alcohol of 65 per cent., and in absolute alcohol; from the latter solution, a double volume of water throws down a colourless semifluid salt, which dries up in the air to a transparent resin, and dissolves in ether and in mineral naphtha.—The *manganese-* and *zinc-salts* are soluble in absolute alcohol.

Sylvates of Potassium.—a. The *normal salt*, $C^{20}H^{29}KO^2$, is formed by boiling sylvic acid with 6 pts. of alcohol and with carbonate of potassium, and is deposited from the filtrate on cooling in delicate white needles, which may also be obtained by mixing the salt γ with alcoholic sylvic acid (Unverdorben; Sievert). It melts to a resin when heated; dissolves very slightly in water, slowly in 20 pts. of alcohol, more freely in hot alcohol; abundantly in warm ether and oil of turpentine, and to a less extent in olive-oil (Unverdorben).—*β.* An *acid salt*, $C^{20}H^{29}KO^2.3C^{20}H^{30}O^2$, is produced by boiling alcoholic potash neutralised with sylvic acid, and solidifies, on cooling, to a crystalline mass, which may be purified by recrystallising and pressing. The same salt is precipitated from alcoholic sylvic acid by an alcoholic solution of potassic acetate. It forms fine silky tufts of delicate needles; decomposes when boiled with water, three-fourths of the acid being precipitated, whilst the normal salt remains in solution (Sievert).—γ. A sparingly soluble *basic salt* appears to be formed by dissolving sylvic acid precipitated by water in caustic potash, and adding more sylvic acid (Rose). Carbonate of potassium added to an ethereal solution of sylvic acid throws down a colourless amorphous salt. (Unverdorben.)

The *silver-salt*, $C^{20}H^{29}AgO^2$, crystallises from alcohol in shining granules on spontaneous evaporation. When boiled with potash and oil of turpentine, it behaves like pinate of silver. Dissolves in 15 pts. of cold, and in a smaller quantity of boiling alcohol, and instantaneously in ether, which takes it up from water when suspended therein. (Unverdorben.)

The *sodium-salt* is obtained in crystals, by boiling alcoholic sylvic acid with excess of sodic carbonate, and cooling the filtrate. (Unverdorben.)

OXYSYLVIC ACID (?)—When an alcoholic solution of sylvic acid is left for some time exposed to the air, or allowed to evaporate slowly, a viscid uncrystallisable substance remains, which melts over the water-bath, losing a little water, and forms, on cooling, a white brittle mass like colophony. This, according to Hesse (Ann. Ch. Pharm. xxix. 141) and H. Rose, is an oxysylvic acid; Hesse found it to contain $C^{20}H^{30}O^4$. Rose however, in one experiment, found that the residue had the same composition as sylvic acid.

SYLVINE, or **SYLVITE.** Chloride of potassium, occurring in cubic crystals about the fumaroles of Vesuvius.

SYLVINOLIC ACID, $C^{25}H^{36}O^4$. (Maly, Wien. Akad. Ber. [2], xliv. 121; Jaresb. 1861, p. 389.)—An acid produced, together with sylvic acid, by saturating an alcoholic solution of abietic acid with hydrochloric acid gas; the sylvic acid then crystallises out, while the sylvinolic acid remains in solution, and is precipitated therefrom by water, as a white flocculent powder, easily soluble in alcohol and in ether. On evaporating either of these solutions, the acid remains as an amorphous pitchy mass, which melts with decomposition at 130°. Sylvinolic acid is dibasic.

The *potassium-* and *sodium-salts* are uncrystallisable, soluble in water and in alcohol. —The *calcium-salt*, $C^{25}H^{34}Ca''O^4$, is a flocculent precipitate.—The *silver-salt*, $C^{25}H^{34}Ag^2O^4$, is a pulverulent precipitate nearly insoluble in ammonia.

SYMBOLS, CHEMICAL. See FORMULÆ (ii. 695), and NOTATION (iv. 136).

SYMMORPHOSIS. A name applied by Liebig (Ann. Ch. Pharm. xxx. 255), to the kind of chemical metamorphosis which consists in the union of several simpler molecules into a molecule of greater complexity: *e.g.*, the conversion of 2 at. potassic cyanide and 1 at. ferrous cyanide into 1 at. potassic ferrocyanide, of 3 at. cyanic acid into 1 at. cyanuric acid, &c.

SYMPATHETIC INK. See INK (iii. 272).

SYMPHYTUM. A genus of plants, belonging to the order *Boraginaceæ*. *S. asperrimum* contains, in 100 pts. of the fresh herb, 88 pts. water, 6 pts. matter soluble in water, 3·2 soluble in dilute potash, 2·6 woody fibre, and 2·3 ash free from carbonic acid. The ash contains, in 100 pts.: 31·3 K^2O, 10·9 Na^2O, 20·5 CaO, 1·2 MgO, 0·4 Al^2O^3, 17·2 SiO^2, 3·9 SO^3, 11·4 P^2O^5 and 3·1 Cl.

The root of comfrey (*S. officinale*) contains a large quantity of vegetable mucilage ($C^6H^{10}O^5$, according to Schmidt), and a small quantity of asparagine.

SYMPLESITE. A mineral supposed to be a ferrous arsenate, found at Lobenstein in Voigtland, in minute, monoclinic, prismatic crystals resembling cobalt-bloom, cleavable parallel to the large lateral face. It has a greenish-blue colour and vitreous lustre, pearly on the cleavage-face; hardness = 2·5 nearly; specific gravity = 2·957; subtransparent to subtranslucent. Heated in a glass tube, it turns brown, and loses 25 per cent. water. On charcoal it emits an alliaceous odour, turns black without melting, and is afterwards magnetic. (Breithaupt, J. pr. Chem. x. 501.)

SYNANTHERIN. See Sinistrin (p. 311).

SYNAPTASE. Syn. with Emulsin (ii. 486).

SYNDESMIDES. Laurent's name for the so-called conjugated compounds.

SYNOVIA. A clear, yellowish, very viscid, alkaline fluid, found in the joints of animals, where it serves the purpose of lubrication. It contains—water 94·85, albumin and extractives 3·51, fat 0·8, salts 1·00. (Frerichs.)

SYNTHESIS, CHEMICAL. The formation of compounds by the union of their elements or proximate constituents. On the synthesis of organic compounds, see Organic Chemistry (iv. 216); also Berthelot (*Chimie organique fondée sur la synthèse*, 2 tomes, Paris, 1860; and Chem. Soc. Qu. J. xvii. 37).

SYNTONIN (συντείνω). *Muscle-fibrin.*—This name was given by Liebig to a substance which can readily be prepared from muscular or contractile tissues of all kinds. Muscle freed from blood, finely minced, and thoroughly washed in the cold until the wash-water no longer gives signs of the presence of albumin, is treated with tenfold its volume of diluted (·1 per cent.) hydrochloric acid, and left to stand for 24 hours. The acid solution, after being strained and filtered, is carefully neutralised with sodic carbonate, and the resulting precipitate filtered off and washed. The operation should be carried on at a low temperature, and pushed forward as speedily as possible, in order to avoid decomposition.

Syntonin thus prepared appears on the filter as a white, opaque, gelatinous mass, readily separating into flakes and pellicles. Composition: C 54·06, H 7·28, N 16·05, O 21·50, S 1·11. It is readily soluble in very dilute hydrochloric acid, in feebly alkaline liquids (such as a solution of sodic carbonate), in baryta-water, and in lime-water. It is quite insoluble in solutions of sodic chloride, &c., at all degrees of concentration.

The hydrochloric acid (·1 per cent.) solution is not coagulated by heat, but the addition in the cold of chloride of sodium, calcium, or ammonium, or of sulphate of sodium or magnesium, produces in dilute solutions a milky turbidity, in concentrated solutions a gelatinous precipitate, which on being boiled separates into flakes. The sodic carbonate (1 per cent.) solution is not coagulated by heat, but is rendered turbid in the cold by sodic chloride, or by a mixture of magnesian sulphate and chloride of ammonium; the turbidity increases when the mixture is boiled, and the froth formed contains opaque flakes. The lime-water solution is not coagulated by heat, but froths freely; and the froth contains flakes, which may be separated on standing. Only a fraction, however, of the syntonin is thus, so to speak, coagulated. In the lime-water solution the chlorides of sodium, ammonium, and magnesium produce in the cold little or no turbidity, on boiling a more or less copious deposit; sulphate of magnesium produces in the cold a slight turbidity, on boiling a flaky deposit; sulphate of sodium produces not even a turbidity, either in the cold or on boiling. A lime-water solution, which has been boiled and allowed to stand, still exhibits these reactions (Kühne, *Protoplasma*). From the alkaline solutions, syntonin may be thrown down by a stream of carbonic anhydride. Although neither the alkaline nor the acid solutions are coagulated by heat, syntonin, when suspended in water and heated for a few minutes to 85°, is altered, and enters into an insoluble form. With strong acetic acid, syntonin forms a turbid gelatinous mass. A solution of syntonin in dilute hydrochloric acid exhibits a specific lævorotatory power of 72° for yellow light.

Although syntonin is most readily obtained from muscle, it may be prepared in many other ways. If fibrin or coagulated albumin be treated with fuming hydrochloric acid, the solution, filtered and diluted with twice its bulk of water, gives a copious deposit, which, when separated and dissolved in water, forms a solution identical in its reactions with an acid solution of syntonin. If a solution of potassic albuminate be precipitated with acetic acid, the washed deposit dissolves in hydrochloric acid of 1 per cent., and the solution is undistinguishable from an acid solution of syntonin. The uncoagulated albumin of hen's eggs, treated with a sufficient quantity of ·1 per cent. hydrochloric acid, forms a solution which, after 24 hours' standing, becomes uncoagulable by heat, and gives all the reactions of syntonin. In fact, all the forms of albumin treated with dilute hydrochloric acid, give rise, in a greater or less extent, to syntonin; and the parapeptone of Meissner, the initial stage of peptonification, cannot, by any of its reactions, be distinguished from syntonin. Lastly, the alkaline solutions of syntonin seem in no way to differ from the solutions of ordinary potassic albuminate.

Syntonin, therefore, is no special muscle-product, though it is more easily and speedily formed out of myosin than out of any other proteid substance. M. F.

SYRIA. A red dye-stuff, occurring in commerce as a dark-red, tasteless, and inodorous powder, which imparts a red colour to water and alcohol, and burns with the odour of horn when heated. According to Vizey (J. Pharm. xxvi. 167), it consists of the incompletely exhausted residue of *Coccus Ilicis*, therefore for the most part of chitin, mixed with coccus-red.

SYRINGA VULGARIS. *Common Lilac.*—The leaves of this plant contain, according to Dumenil (Trommsd. N. J. xi. 117), uncrystallisable sugar.—Ludwig (Arch. Pharm. [2] xci. 289) found mannite in them, also in the young branches. Bernays and Kromayer (*infra*) found in the leaves, branches, and bark, a glucoside called *syringin*.—Meillet (Ann. Ch. Pharm. xl. 319) obtained from the leaves and green seed-capsules, a crystallisable substance, which he designates as *lilacin*; it resembles syringin in all its properties, excepting in having a bitter taste, and being insoluble in water. According to Mulder (J. pr. Chem. xxxii. 172), the waxy substance contained in the leaves has the composition of ordinary wax. The odoriferous principle of the flowers may be obtained (according to Favret, J. Chim. méd. xiv. 212), by extraction with ether, as a viscid oil, composed of a waxy body and a mobile oil.

SYRINGENIN. $C^{13}H^{22}O^5.H^2O$.—A substance obtained, together with fermentable sugar, by warming syringin with dilute sulphuric or hydrochloric acid. It is deposited in viscid cohering flocks, and forms, after washing with water, a light rose-coloured amorphous mass, which becomes anhydrous at 100°, melts at 170°—180°, is insoluble in water and in ether, dissolves with cherry-red colour in alcohol, and separates from this solution, on evaporation, as a light cinnamon-coloured powder, composed of transparent globules. It reacts with acids like syringin. (Kromayer.)

SYRINGIN. $C^{19}H^{28}O^{10}.H^2O$. (Bernays, J. pr. Chem. xxv. 121.—Kromayer, Arch. Pharm. [2] cviii. 7; cix. 18, 216; cxiii. 19; Jahresb. 1862, p. 484; 1863, p. 592.)—This compound, discovered by Bernays in 1841, and more completely investigated by Kromayer, occurs in the bark of the lilac, more abundantly in March than in April, not in the leaves or in the half-ripe fruit, and only in traces in the leaf-buds. It disappears as the season advances, its place being apparently supplied by syringopicrin (Kromayer). Ligustrin from privet-bark (iii. 694) is (according to Kromayer) identical with syringin. Meillet's lilacin (*supra*) is probably also the same substance.

To prepare syringin, the bark is exhausted with boiling water; the extract precipitated with basic acetate of lead; the filtrate treated with sulphydric acid; and after removal of the sulphide of lead, evaporated to a thin syrup, which solidifies in the course of a day to a crystalline pulp. This mass is purified by stirring it up with cold water, then pressing, and recrystallising it from boiling water, with aid of animal charcoal. The syringin dissolved in the wash-waters is obtained by evaporating the liquid, and agitating the residue with alcohol, which takes up the syringin. (Bernays; Kromayer.)

Syringin crystallises from alcohol in long, colourless, transparent needles, containing 4·5 per cent. (1 at.) water, which they give off at 115°, leaving anhydrous syringin, $C^{19}H^{28}O^{10}$, which melts at 212° to a colourless liquid, and solidifies on cooling to an amorphous, transparent, hard, friable, tasteless, neutral mass (Kromayer). Ligustrin from privet melts at 185°—190°. (Kromayer.)

Syringin dissolves sparingly in cold, easily in hot *water*; it is soluble also in *alcohol*, but not in ether; it does not precipitate metallic salts.

Decompositions.—1. Syringin, when *heated*, decomposes below its melting-point, giving off an odour of caramel, and burning away.—2. The aqueous or alcoholic solution of syringin acquires a fine dark-blue colour when mixed with an equal volume of *oil of vitriol*; with a larger quantity of oil of vitriol, the colour changes to a beautiful violet, and the liquid on standing deposits blue, and on addition of water, grey-blue flocks, which dissolve with cherry-red colour in alcohol and in ammonia.—3. When cautiously heated with fuming hydrochloric acid, it dissolves without coloration, but on boiling, the solution assumes a light violet-red colour, and deposits blue flocks.—4. An aqueous solution of syringin through which *chlorine-gas* is passed acquires a red-brown colour, but after a while becomes quite colourless. At the same time an acid is formed, having a bitter irritating taste, and assuming a dark-blue colour when mixed with ferric chloride.—5. Syringin dissolves quickly in strong *nitric acid*, forming a deep blood-red solution.

6. When aqueous syringin is heated with dilute *hydrochloric acid*, the solution becomes milky, and deposits adhering lumps of syringenin, whilst fermentable sugar remains dissolved:

$$C^{19}H^{28}O^{10} + H^2O = C^{13}H^{18}O^5 + C^6H^{12}O^6.$$

100 pts. crystallised syringin yielded 61·77 pts. air-dry syringenin and, on the average, 41 pts. sugar (calc. 62·67 pts. hydrate of syringenin and 41·47 sugar: Kromayer).

Syringin does not reduce either *cuprate of potassium* or *nitrate of silver*, and is not altered by *alkalis*. (Kromayer.)

SYRINGOPICRIN. This substance remains in the alcoholic mother-liquor from which syringin has crystallised, and may be extracted therefrom by animal charcoal. By treating the charcoal with hot alcohol (after washing it with warm water), a solution is obtained, which yields by evaporation (after being again treated with charcoal) a yellowish bitter substance, which is soluble in water and in alcohol, but not in ether; is precipitated by tannic acid, but not by basic acetate of lead; and does not reduce an alkaline cupric solution till it has been boiled with dilute sulphuric acid. (Kromayer, *loc. cit.*)

SYRUP. A concentrated solution of sugar. In the sugar-manufacture, the term is applied especially to the mother-liquor remaining after the cane-sugar has crystallised out. In pharmaceutical language, it is applied to solutions of sugar, either in pure water, in the decoction or infusion of any medicinal substance, in vinous infusions or in pressed and fermented fruit-juices.

SZAJBELYITE. A hydrated borate of magnesium, occurring imbedded, in rounded grains and microscopic needles, in the fine-grained limestone of the metalliferous deposits of Rezbanya in Hungary, and remaining behind when the limestone is dissolved in dilute acids. Specific gravity of the needles = 2·7, of the grains = 3·0. It gives off water when heated, but reabsorbs it after cooling. Before the blowpipe, it splits and swells up on the edges with strong incandescence, then melts to a tumefied and finally horny brownish-grey mass; colours the flame red to yellow-red. In phosphorus-salt it dissolves slowly to a clear glass, yellowish while hot, colourless after cooling; in borax, after prolonged effervescence, to a clear bead having a faint reddish-grey colour, but remaining colourless after exposure to the reducing flame. (K. F. Peters, Wien. Akad. Ber. xliv. [2] 143; xlvii. [2] 347; Jahresb. 1862, p. 1029.)

The following analyses by A. Stromeyer (Jahresb. 1863, p. 836), show that the composition of the needles is $5MgO.2B^2O^3.\frac{4}{3}H^2O$, and that of the grains, $5MgO.2B^2O^3.\frac{8}{3}H^2O$:

		B^2O.	MgO.	Fe^2O^3.	H^2O.	Cl.	Quartz.	Charcoal and MnO.		
Needles	.	36·66	52·49	1·66	6·99	0·49	0·20	trace	=	98·49
Grains	.	34·60	49·44	3·20	12·37	0·20	. .	. .	=	99·81

SZESKO. The Hungarian name of native sodic carbonate.

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TABASHEER. Hydrated silica, occurring in stony concretions in the joints of the bamboo. It resembles hydrophane, and when thrown upon water does not sink till completely saturated therewith. It is the least refractive of all known solids, its index of refraction, for the yellow ray, being 1·115. Rost van Tonningen (Jahresb. 1860, p. 531) found in tabasheer from Java, 86·39 per cent. silica soluble in potash, 0·42 ferric oxide, 0·24 lime, 4·81 potash, 0·51 organic matter, and 7·63 water.

TABERGITE. A chloritic mineral from Taberg in Wermland, Sweden; closely resembling clinochlore in external aspect and in reactions; and containing, according to Svanberg (Berz. Jahresb. xx. 235), 35·76 per cent. silica, 13·03 alumina, 30·00 magnesia, 6·34 ferrous oxide, 1·64 manganous oxide, 2·07 potash, 11·76 water, and 0·67 fluorine. According to Descloizeaux (Ann. Min. xi. 280), it is optically biaxial, like clinochlore, and differs in composition from that mineral only in consequence of admixtures.

TABULAR SPAR. *Wollastonite.* Native silicate of calcium, $Ca''SiO^3$. (See Silicates, p. 252.)

TACAMAHAC. *Gummi Takamahak.*—A resin formerly used for fumigation and for plasters. There are two varieties of it:—*a.* West Indian tacamahac, from *Elaphrium tomentosum*, Jacq. (*Fagara octandra*, L.) and *E. excelsum*, Kth., trees belonging to the order *Burseraceæ*, and indigenous in Mexico, the West Indies, and South America. The resin exudes from the bark, and hardens on exposure to the air. It forms reddish or brownish lumps, having a bitter aromatic taste, imperfectly soluble in alcohol and alkalis, perfectly soluble in ether and in oils, both fat and volatile.—*β.* The East Indian variety, from *Calophyllum inophyllum*, L. (according to Lindley from *C. Calaba*, L.), an East Indian tree belonging to the order *Clusiaceæ*, is very rare. It is a greenish-yellow or orange-coloured, soft, resinous mass, which gradually hardens, has an agreeable lavender-like odour, and aromatic somewhat bitter taste; melts easily, and dissolves completely in alcohol.

TACHYAPHALTITE. A mineral discovered by Weibye (Pogg. Ann. lxxxviii. 160), at Krageröe in Norway, where it occurs imbedded in granite veins in the gneiss. According to Berlin, it contains 34·58 per cent. silica, 38·96 zirconia, 12·32 thorina(?) 3·72 ferric oxide, 1·85 alumina, and 8·49 water. It forms dimetric crystals, like those of zircon, being combinations of the prisms ∞P and $\infty P \infty$ with two octahedrons—one of 110° (terminal edge), the other of 50°. Cleavage not very distinct. Fracture conchoïdal. Hardness = 5·52. Specific gravity = 3·6. Lustre submetallic to vitreous. Colour dark reddish-brown. Streak dirty-yellow. Subtranslucent. Heated in a tube, it gives off water with slight fluorine reaction. Before the blowpipe it becomes dirty-white, but does not melt. In borax it dissolves with difficulty; with soda, on platinum, it forms a dirty yellowish-brown slag.

TACHYDRITE. $Ca''Mg''^2Cl^6.12H^2O$ or $Ca''Cl^2.2Mg''Cl^2.12H^2O$.—This mineral occurs in the saline deposits of Stassfurt, in roundish, yellow, transparent to translucent lumps, which are imbedded in compact anhydrite, and contain small crystals of the latter enclosed within themselves. It cleaves distinctly in two directions. Deliquesces quickly when exposed to the air.

TACHYLYTE. *Conchoïdal Augite.*—A silicate occurring in basalt on the Säsebühl near Daansfeld in Hanover, and containing (according to Schnedermann) 55·74 per cent. silica, 12·40 alumina, 13·06 ferroso-ferric oxide, 7·28 lime, 5·92 magnesia, 3·88 soda, 0·60 potash, 0·19 manganous oxide, and 2·73 water. It is amorphous, with conchoïdal, even or uneven fracture; black and opaque, with waxy lustre and dark-grey streak; brittle and somewhat magnetic; hardness = 6·5; specific gravity = 2·565–2·593. Before the blowpipe it melts very easily, and with intumescence, to a blistered, brownish-green, magnetic glass, and gives with borax the reaction of iron.

Hyalomelane, a mineral occurring in the porous basalt of the Vogelsgebirge in Hesse, is usually regarded as identical with tachylyte, but according to Hausmann (*Handb. d. Mineral.* ii. 546), it is a distinct species. According to an analysis by C. G. Gmelin (Pogg. Ann. xlix. 234), it contains:

SiO^2.	TiO^2.	Al^2O^3.	FeO.	CaO.	MgO.	Na^2O.	K^2O.	MnO.	Water and ammonia.		
50·22	1·41	17·84	10·26	8·25	3·37	5·18	3·86	0·40	0·50	=	101·29

Nearly allied to it is a mineral from the Wetterau, likewise analysed by Gmelin (Leonhard's N. Jahrb. f. Mineral., 1840, p. 549), which has a specific gravity of 2·705, does not gelatinise with acids, and is not decomposed even by boiling with strong sulphuric acid; also a scoriaceous augite, described by D. L. G. Karsten, and analysed by Klaproth (*Beiträge*, iv. 190), from a limestone deposit at Guiliane in Sicily. (Handw. d. Chem., viii. 467.)

TÆNIIN, or *Koussin.*—A resinous substance, supposed to constitute the active principle of kousso-flowers (the flowers of *Brayera anthelmintica*). It is extracted by digesting the flowers with strong alcohol containing a little potash, and is obtained by evaporation as a resinous mass, or as a white powder having a bitter nauseous taste. It melts at about 100°, is nearly insoluble in water, soluble in 1300 pts. spirit of 45 per cent. at 17°, and in 12 pts. alcohol of 90 per cent.; it dissolves in ether in nearly all proportions, and with tolerable facility in alkalis, whence it is precipitated by acids. (Pavesi, Buchn. N. Repert. viii. 325.—Bedall, *ibid.* 546.)

TAGILITE. A basic cupric phosphate, $\overline{Cu}{}^3P^2O^8.Cu''H^2O^2$, from Nischne-Tagilsk (iv. 561).

TAGUA-NUT. The fruit of *Phytelephas macrocarpa*, worked as "vegetable ivory."

TA-HONG. [illegible] —containing ferric oxide, used in China as a red enamel [illegible]

TAIGU WOOD. A wood from Paraguay, resembling guaiacum-wood in appearance and specific gravity. It has a greenish-brown colour when fresh; becomes covered, on exposure to the air, with a greenish-yellow crystalline powder; and exhibits under the microscope yellow oblique prisms, together with shining, colourless, thin, six-sided tables: the latter are not altered by alkalis; the former, which consist of taiguic acid, are reddened thereby. Strong boiling alcohol extracts from it 13·7 per cent. of a mixture of taiguic acid with resinous and waxy substances. The wood, after drying in hydrogen-gas, yields, when boiled with water, 5·7 per cent. of a gum-resin smelling like benzoin, after which alcohol again extracts from it 2·5 per cent. of resinous substance.

TAIGUIC ACID. (Arnaudon, Cimento, vii. 37; Jahresb. 1858, p. 264.)—This acid, which occurs in the cold alcoholic extract of taigu wood (*supra*), is freed from admixed resins by repeated treatment with alcohol, and from waxy matters by ether: the solution is then evaporated, and the residue dried: 100 pts. of the wood yield 2 pts. of the acid.

Taiguic acid crystallises in oblique prisms having a fine yellow colour: it is tasteless and inodorous; but when rubbed, emits an unpleasant odour, and becomes electric: it melts at 135°, and sublimes at 180°. It is but very slightly soluble in water, even at the boiling heat (about 0·001); but when heated with water to 140° in a sealed tube, it dissolves in larger quantity, and crystallises on cooling. Acetone, ethers, benzene, and strong alcohol dissolve it freely. It contains 70·9 per cent. carbon, 5·9 hydrogen, and 23·2 oxygen, agreeing with the empirical formula C^4H^4O.

Taiguic acid unites with bases, forming crystallisable salts, from which it is separated unaltered by the stronger acids. With the alkalis it forms easily soluble salts having a deep red colour, the production of which is quite independent of atmospheric oxygen; hence taiguic acid forms a very delicate test for the presence of alkalis. The neutral solutions of the alkaline taiguates form, with neutral acetate of lead, an amorphous scarlet precipitate, which, in contact with water, gradually becomes crystalline and reddish-yellow; it is slightly soluble in water, more soluble in alcohol, and is obtained in pointed crystals by evaporation of the alcoholic solution.—Nitrate of silver forms, in neutral solutions of the alkaline taiguates, a cinnabar-coloured precipitate, which is decomposed by exposure to light, is nearly insoluble in water and in ether, moderately soluble in alcohol, freely in ammonia.

TAKOURAVE. Syn. with NEPHRITE (iv. 31).

TALC. $4Mg''O.5SiO^2.\frac{4}{3}H^2O$.—This mineral occurs both crystallised and massive; the massive variety is called steatite,* and was formerly regarded as a distinct species; but it has the same composition as crystalline talc.

Talc usually forms lamellar crystals, which cleave perfectly in one direction, but are too incompletely developed to admit of an exact determination of their crystalline system; they are, however, optically biaxial, and, besides the principal cleavage, exhibit also traces of cleavage in two directions obliquely inclined to one another. The crystals are of various sizes, forming plates, laminæ, and scales, and are sometimes elongated in one direction. They also occur aggregated, in crystallo-laminar, radio-laminar, or scaly groups, which in larger masses often exhibit a true slaty structure (talcose slate). The lamellæ are very flexible but not elastic, and unctuous to the touch. Talc is very soft, its hardness being, in fact, adopted as the unit of the scale. Specific gravity = 2·6 to 2·8. It is colourless, white, grey, greenish-white and greenish-grey, apple-green, leek-green, and yellowish-white to yellowish-grey, transparent (in thin lamellæ) to merely translucent on the edges, and has a waxy lustre, nacreous on the perfect cleavage-faces. When heated before the blowpipe, it glows brightly, usually exfoliates and burns hard (to a hardness of 6), but does not fuse; with phosphorus-salt it yields a skeleton of silica, and when moistened with cobalt-solution, and ignited, it becomes pale-red. It is insoluble in acids both before and after ignition.

Compact steatite (*Speckstein* of the Germans), which occurs massive, imbedded in kidney-shaped and nodular lumps, also as pseudomorphs after quartz and dolomite, has an uneven to splintery fracture, a greasy feel, and does not adhere to the tongue. Its specific gravity and hardness are, for the most part, the same as those of talc: the hardness, however, is sometimes rather greater (= 1·5). It is white, grey, yellow, red, green, dull, opaque to translucent on the edges. When heated in a glass tube, it gives off a little water; before the blowpipe it does not melt, but burns to a degree of hardness sufficient to scratch glass; when ignited with cobalt-solution, it becomes pale red. It is decomposed by boiling sulphuric acid, differing in that respect from crystalline talc.

Potstone, or *Lapis ollaris*, is a coarse dark-coloured steatite, more or less impure.

Pure talc, $4Mg''O.5SiO^2.\frac{4}{3}H^2O$, contains 62·14 per cent. silica, 32·92 magnesia, and 4·94 water. The numerous analyses of the mineral in its several varieties exhibit but slight deviation from this composition—viz., from about 62 to 64 per cent. silica, 28 to 33 magnesia, and 2·5 to 5 water, with from 0·5 to 7 per cent. ferrous oxide replacing part of the magnesia, and occasionally small quantities of alumina, lime, &c., which must be regarded as impurities. Some varieties appear to be anhydrous, or to contain but very little water; but this result is perhaps due to defective analysis, as the water is expelled only at a very strong red heat. (For the individual analyses, see Rammelsberg's *Mineralchemie*, p. 517.)

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* Soapstone (also called steatite) is a mineral of different composition—viz., silicate of magnesium and aluminium (p. 324).

Talc is a very widely diffused mineral, some of its varieties (especially common talc, potstone, and steatite) forming extensive beds in regions of crystalline rocks. Apple-green talc occurs in Unst, one of the Shetland Isles; also on the Greiner Mountain in Salzburg, and in the Valais, &c. Potstone occurs in the Valais and the Grisons, and at Wald in Styria. Extensive beds of steatite occur in various parts of the New England States—also in New Jersey, Pennsylvania, &c.

Green talcose minerals occur at Fahlun in Sweden, and at Gastein in the Tyrol. A white, large-laminated, and radio-laminated talc from Pressnitz, in Bohemia, contains about 68 per cent. silica, 26 magnesia, 1·2 to 1·6 ferrous oxide, and 4·1 water. (Scheerer.)

Slabs of steatite are extensively employed as firestones in furnaces and stoves. It may be turned in a lathe, and formed into tubes by boring. When ground, it is used for diminishing friction. It is also employed in the manufacture of some kinds of porcelain. Venetian talc is used for removing oil-stains from woollen cloths, &c. (Dana, ii. 277.)

TALC, INDURATED. The harder varieties of steatite.

TALC, WHITE, from China; syn. with Agalmatolite (i. 60).

TALC-ALUM. A term sometimes applied to magnesio-aluminic sulphate (p. 583).

TALCAPATITE. A variety of apatite containing magnesia, occurring in six-sided crystals, grouped or single, in the chlorite-slate of the Schischimskan Mountains, near Slatoust in the Ural. According to Hermann (J. pr. Chem. xxxi. 101), it contains 37·50 per cent. lime, 7·74 magnesia, 39·02 phosphoric acid, 2·10 sulphuric acid, 0·91 chlorine, 2·23 fluorine (and loss), 1·00 oxide of iron, and 9·50 insoluble matter. The soluble portion may be represented approximately by the formula $3Ca^3P^2O^8.Mg^3P^2O^8$; but it is probably only an impure apatite, the magnesia being derived from the gangue.

TALC-CHLORITE. Syn. with Clinochlore.

TALC-IRON-ORE. *Magnesian Iron-ore. Talkeisenerz. Tesseranus magnesifer.*—This name is applied by Breithaupt (*Handb. d. Mineralogie*, iii. 778) to an iron-ore from the State of New York, consisting (according to Plattner) of ferrous oxide with much magnesia, a somewhat considerable quantity of titanic acid, and a small quantity of alumina, but no chromium. It forms cubo-octahedrons, fissured internally, but exhibiting only traces of cleavage parallel to the cubic and octahedral faces. It is opaque, iron-black with black streak, and nearly semimetallic lustre. Hardness = 6·0. Specific gravity = 4·0 to 4·5. Very slightly magnetic. Behaves before the blowpipe like titaniferous iron-ore.

TALC-IRONSTONE. *Talkeisenstein.*—Breithaupt's name for a magnetic iron-ore from Sparta in New Jersey, having the ferrous oxide partly replaced by magnesia. It is slightly magnetic, and has a density of 4·41 to 4·42. Allied to this is the magnesiferous magnetic iron-ore occurring in imperfect octahedrons in the slates of the Mourne Mountains in Ireland, and containing, according to Andrews (J. pr. Chem. lvii. 376), 71·41 per cent. Fe^2O^3, 21·59 Fe^2O, and 6·45 MgO.—Also Rammelsberg's magnoferrite from Vesuvius (iii. 784).

TALC-GARNET. *Talkgranat. Talkthongranat.* Magnesian garnet from Arendal in Norway (ii. 772).

TALCITE, or **TALXITE.** A mineral from Wicklow in Ireland, allied to nacrite (iv. 1).

TALCOÏD. This name was applied by Naumann to the white laminated talc from Pressnitz in Bohemia (*supra*).

TALCOSE SLATE. A dark slaty rock, having a somewhat greasy feel, and consisting largely of talc, intimately mixed with felspar and quartz.

TALLICOONAH-OIL. Syn. with Carapa-oil (i. 749).

TALLINGITE. An oxychloride of copper, allied to atacamite, from the Botallack mine in Cornwall. It forms greenish-blue, thin, somewhat crystalline crusts, composed of small spherules. Hardness = 3. Specific gravity = 3·5. It is insoluble in water, easily soluble in dilute acids and in ammonia, and turns green, with loss of water, at 100°. It contains 66·24 per cent. cupric oxide, 11·33 chlorine, and 24·16 water (= 101·73), besides traces of carbonic acid, arsenic, alumina, and sodic chloride: whence the formula, $Cu''Cl^2.4Cu''H^2O^2.4H^2O$ (Church, Chem. Soc. Qu. J. xviii. 77). For atacamite, Church calculates the formula $Cu''Cl^2.3Cu''H^2O^2.H^2O$. (Compare i. 429.)

Another cupric oxychloride from the same mine, called *botallackite*, occurring in thin pale mountain-green crusts, of specific gravity 3·6, was found to contain 66·25 per cent. $Cu''O$, 14·76 Cl, and 22·45 H^2O (= 103·22), whence the formula $Cu''Cl^2.3Cu''H^2O^2.3H^2O$. A blue cupric oxychloride, also from the same mine, appeared, from a preliminary analysis, to consist of $Cu''Cl^2.6Cu''H^2O^2.6H^2O$. (Church, *ibid.* 212.)

TALLOW. This name is applied to the harder and less fusible fats, occurring chiefly, though not exclusively, in the animal kingdom, the most common being beef and mutton tallow. The most solid of the vegetable fats are cacao-fat, from *Theobroma Cacao*; Chinese tallow, from the berries of *Stillingia sebifera*; myrica-tallow, from the berries of *Myrica cerifera* (which, however, is rather a wax); virola-tallow, from the shelled almonds of *Myristica sebifera*; and piney-tallow, from the fruit of *Valeria indica*. Cocoanut-fat is also frequently called a tallow, though it has rather the consistence of butter. (See the names of the several plants in this Dictionary; also *Gmelin's Handbook*, xvi. 385—400.)

Animal tallow consists chiefly of stearin, palmitin, and olein, the stearin predominating, but varying with the species of the animal (*e.g.*, mutton and deer tallow are mostly harder and less fusible than beef-tallow), and with the age, mode of feeding, &c. The tallow is separated from the cellular tissue in which it is enclosed (the entire mass constituting suet) by melting. This operation is performed at the lowest possible temperature, and is much facilitated by the addition of dilute sulphuric acid (1 pt. oil of vitriol and 20 pts. water to 100 pts. tallow). The melted tallow is white, if pure; a less pure tallow, which has a yellowish colour, may be bleached by exposure to light and air; more rarely, the bleaching is effected by the use of chemical reagents—*e.g.*, by heating 100 pts. of the tallow with 1 pt. sulphuric acid and ½ pt. red chromate of potash, or 200 pts. tallow with 1 pt. nitric acid and 1 pt. oil of vitriol.

Tallow, especially that of the ox and sheep, is largely used for the manufacture of soap and candles; in smaller quantity also in pharmacy.

TALMI GOLD, an alloy used for the manufacture of trinkets, contains, according to Sauerwein (Dingl. l. clxx. 154), 86·4 per cent. copper, 12·2 zinc, 1·1 tin, and 0·3 iron.

TA-LOU. The Chinese name for a glass flux, consisting chiefly of silicate of lead with a little copper, used as an enamel colour on porcelain. (Ebelmen and Salvétat, Ann. Ch. Phys. [3] xxxv. 344.)

TALTALITE. The name given by Domeyko (Jahresb. 1863, p. 815) to a black or brown-black crystalline mineral from a mine in the desert of Atacama, containing 44·5 per cent. CuO, 2·4 CaO, 0·8 MgO, 16·2 Al^2O^3, 11·3 Fe^2O^3, 20·8 SiO^2, 0·7 Cl, and 2·5 loss by ignition (= 99·2). According to Ulex (*ibid.* 1865, p. 888), it is a fine-grained mixture of atacamite, malachite, red hæmatite, and calcspar, intersected by crystals of tourmalin.

TAMARINDS. *Fructus Tamarindarum.*—The pulpy mass contained in the pods of *Tamarindus indica*, a leguminous tree growing in the East and West Indies, in Egypt, and in Arabia. It has a faint vinous odour and agreeably acid taste. Vauquelin (Ann. Chim. v. 92) found in East Indian tamarinds, sugar, gum, pectic acid, malic, citric and tartaric acids, acid tartrate of potassium, and cellulose. Scheele did not find citric acid. According to Gorup-Besanez (Buchn. Repert. lxviii. 260), tamarinds likewise contain acetic and formic acids.

TAMARITE. *Chalcophyllite. Copper-mica* (in part).—A basic cupric arsenate, occurring in rhombohedral crystals, also foliated, massive, and in druses. Principal axis of rhombohedron = 2·5536. Angle R : R (terminal) = 69° 48′; oR : R = 108° 4′. Observed combination, oR . R, also with +2R, $-\frac{1}{2}$R, and ∞R. Cleavage highly perfect parallel to oR, which plane is sometimes triangularly striated. Hardness = 2. Specific gravity = 2·4 to 2·66. Lustre pearly on the base, vitreous or subadamantine on the other faces. Colour emerald- or grass-green to verditer-green. Streak somewhat paler. Fracture scarcely observable. Sectile. When heated it decrepitates and exfoliates. Before the blowpipe it yields a scoriaceous mass enclosing a button of copper.

Analyses.—*a*, by Chenevix (Phil. Trans. 1801).—*b*. Specific gravity = 2·435 (Hermann, J. pr. Chem. xxxiii. 294).—*c*, *d*. Specific gravity = 2·659 (Damour, Ann. Ch. Phys. [3] xiii. 404):

	As^2O^5.	P^2O^5.	CuO.	FeO.	Al^2O^3.	H^2O.		
a.	21	. .	58	. .	. .	21	=	100
b.	17·51	. .	44·45	2·92	3·93	31·19	=	100
c.	19·35	1·29	52·92	. .	1·80	23·94	=	99·30
d.	21·27	1·56	52·30	. .	2·13	22·58	=	99·84

These widely different results cannot be reduced to a single formula:

a may be approximately represented by $8CuO.As^2O^5.13H^2O = Cu^3As^2O^8.5CuH^2O^2.8aq.$
c and *d* „ „ $8CuO.As^2O^5.15H^2O = Cu^3As^2O^8.5CuH^2O^2.10aq.$
b „ „ $8CuO.As^2O^5.23H^2O = Cu^3As^2O^8.5CuH^2O^2.18aq.$

The principal Cornish localities of this mineral are the copper mines of Tingtang, Huel Gorland, and Huel Unity, near Redruth. It occurs also crystallised in iron-ore at Sayda in Saxony, in minute crystals at Herrengrund in Hungary, and at Moldawa in the Bannat. It is sometimes found altered to chrysocolla.

TAMARIX. From the flowers of the French tamarisk (*Tamarix gallica*), a crystalline iridescent substance may be obtained, by exhaustion with alcohol and evaporation (Landerer). The leaves contain a large quantity of potassic sulphate. *T. laxa* grows chiefly on the Kirghis Steppe: 100 pts. of the young air-dried plant yield 33·7 per cent. ash, containing 12·5 per cent. sodic carbonate, 52·0 sodic chloride, 1·6 sodic sulphate, and 3·0 potassic sulphate, together with 38·8 pts. insoluble salts. (Göbel.)
Tamarix mannifera yields, in consequence of the puncture of an insect (*Coccus manniferus*), a saccharine substance, the so-called *Manna of Sinai*, which is a yellow syrup containing 55 per cent. cane-sugar, 25 inverted sugar, 20 dextrin, &c. (Berthelot, Compt. rend. liii. 583.)

TAMTAMS, or *Gong-gongs*.—Chinese musical instruments having the form of a kettle-drum, and sounded by beating them with a stick covered with leather. According to Klaproth, they are formed of an alloy of 78 pts. copper to 22 pts. tin. According to Genth (Mitth. d. Gewerbevereins, f. Hannover, 1859, p. 106), they consist of 80 per cent. copper and 20 per cent. tin. According to Julien (Compt. rend. xxiv. 1069), the Chinese alloy the copper for these instruments, and for cymbals, &c., with ½ pt. of tin.

TANACETIC ACID. An acid said by Peschier (J. Chim. méd. iv. 58), to exist in the flowers of the common tansy (*Tanacetum vulgare*). It is crystalline, soluble in water, forms crystallisable salts with potash and soda, and precipitates the solutions of calcium, barium, zinc, lead, silver, copper, and mercury.

TANACETIN. A bitter substance obtained from the leaves and flowers of tansy. It is prepared in the same manner as absinthin from wormwood (i. 2), and forms a yellowish-white, granular, inodorous mass, easily soluble in ether, sparingly in alcohol, still less in water. The solution has a bitter and rather sharp taste, and is precipitated by plumbic, ferric, and mercurous salts, not by tannic acid. (Fromberg, Geig. Magaz. viii. 35.—Leroy, J. Chim. méd. xxi. 357.)

TANACETUM VULGARE. *Tansy.*—The leaves of this plant contain volatile oil, a bitter extractive matter called tanacetin (*supra*), tannin, sugar, malic acid, and other substances. The flowers contain the same constituents, but are richer in volatile oil, and (according to Peschier) they also contain tanacetic acid. The seeds contain volatile oil, fat oil, and a bitter substance.

The volatile oil of tansy, obtained by distilling the leaves or flowers with water, has a specific gravity of 0·92 to 0·93, dissolves easily in alcohol of specific gravity 0·85, thickens on exposure to the air, dissolves in iodine, but is not sensibly acted upon by it. When distilled with chromate of potassium and sulphuric acid, it yields a volatile crystalline body, having the composition of ordinary camphor (Persoz, Compt. rend. viii. 433; Vohl, Pharm. Centralbl. 1853, p. 318). It is decomposed and dissolved by nitric and by sulphuric acid.

TANAH-AMPO. A plastic earth, occurring in Java, and used by the natives as food, after being dried over a charcoal-fire. (Mohnike, J. Chim. méd. iv. 58.)

TANGHINIA MADAGASCARIENSIS. A shrub indigenous in Madagascar, the kernels of which contain, besides fat oil and the ordinary plant-constituents, a crystallisable substance called tanghin-camphor or tanghinin. To prepare this substance, the almonds are freed from oil by pressure, then exhausted with ether, and the ethereal solution is left to evaporate. Tanghinin then remains behind, and may be obtained, by solution in alcohol and spontaneous evaporation, in colourless, transparent, shining scales, which effloresce on exposure to the air. It has a sharp bitter taste, and afterwards produces a feeling of constriction in the throat. It melts to a resin when gently heated, but is not volatile. It dissolves in acetic acid, without entering into combination, and is coloured yellow by other acids and by alkalis. The alcoholic solution forms white precipitates with lead-, mercury-, and silver-salts. Tanghinin is very poisonous, quickly producing fatal effects.

TANGIWAITE. A variety of nephrite from Tangiwai in New Zealand. (Jahresb. 1864, p. 351.)

TANKITE. A mineral from Norway resembling chiastolite: specific gravity = 2·936. (Breithaupt, Schw. J. 1829, p. 246.)

TANNASPIDIC ACID. $C^{26}H^{29}O^{11}$ (?). (Luck, Pharm. Centr. 1851, p. 667.)—An acid contained, together with pteritannic acid, in the root of the male fern (*Aspidium Filix mas*). The method of extracting these acids and separating them with ether has been already described (iv. 745). The impure tannaspidic acid left undissolved by the ether is purified by solution in alcohol, and evaporation in a retort filled with hydrogen.

Tannaspidic acid forms a black-brown, shining, amorphous mass, triturable to a red-brown powder. It is insoluble in water, ether, oil of turpentine, and fixed oils, easily soluble in strong alcohol, soluble also in warm acetic acid. The alcoholic solution evaporated by heat, in contact with the air, leaves a residue no longer soluble in alcohol. Strong sulphuric acid dissolves it, forming a dark-green liquid, which soon becomes brown-red on the surface. Nitric acid dissolves and decomposes it. With chlorine it forms substitution-products.

Tannaspidic acid dissolves easily in potash or ammonia, forming a dark-brown solution, which quickly absorbs oxygen, especially when warmed, acquiring a brown-red colour: acids added to the latter solution throw down a black powder. The alcoholic solution of tannaspidic acid is precipitated by chloride of barium, chloride of calcium, acetate of copper, nitrate of silver, and chloride of platinum,—also, after addition of ammonia, by zinc-, mercury-, and tin-salts. Ferric chloride colours the alcoholic solution green, and on addition of ammonia a green precipitate is formed. The solution of tannaspidic acid precipitates an alcoholic solution of isinglass, but not a solution of tartar-emetic.

By treating the alcoholic solution of the acid with neutral acetate of lead, a precipitate is formed, which dries up to a black shining mass, containing on the average 43·4 per cent. carbon, 3·6 hydrogen, 22·3 oxygen, and 30·60 plumbic oxide, agreeing approximately with the formula $C^{26}H^{26}Pb''O^{11}$, which requires 43·2 per cent. C, 3·6 H, 22·2 O, and 31·0 PbO.

Chlorotannaspidic Acids.—When dry chlorine-gas is passed over dry tannaspidic acid, a substitution-product is formed, containing 2 at. chlorine, and yielding on trituration a cinnamon-brown powder, having a fruity odour and sour astringent taste, soluble with brown colour in alcohol and aqueous alkalis, but insoluble in water, ether, oil of turpentine, and fixed oils. Tannaspidic acid suspended in water is converted by chlorine or by hypochlorous acid into a product containing 3 at. chlorine; and the air-dried acid, treated with moist chlorine-gas, yields a product containing 4 at. chlorine.

Ethyl-tannaspidic Acid.—The alcoholic solution of tannaspidic acid turns red when boiled with hydrochloric acid, and water added to the solution throws down a red substance.

TANNECORTEPINIC ACID. $C^{28}H^{28}O^{12}$? (Kawalier, Wien. Akad. Ber. xxix. 10.)—An acid resembling the tannic acids, occurring, about Easter-time, in the bark of Scotch fir-trees from 20 to 25 years old. To prepare it, the bark is exhausted with alcohol; the extract left on evaporation is treated with water; the clear aqueous solution is repeatedly precipitated with neutral lead-acetate, a lead-salt mixed with resin then remaining in solution; the clear solutions are precipitated with basic lead-acetate; the washed precipitate is suspended in water, and decomposed by sulphydric acid; and the liquid is concentrated in a stream of carbonic anhydride. Tannecortepinic acid is then deposited in crusts, which yield by trituration a reddish-brown powder having an astringent taste. It is soluble in water, and the solution, warmed with sulphuric or hydrochloric acid, yields a red precipitate having nearly the same composition as the acid, together with a very small quantity of sugar. The aqueous solution of the acid mixed with ferric chloride, acquires a greenish colour, changing to red-brown on standing, and afterwards deposits a blackish-green precipitate.

TANNENITE. A sulphide of copper and bismuth, $Cu^{2}S.Bi^{2}S^{3}$, occurring at Tannenbaum, in the Erzgebirge (ii. 77); also, according to Domeyko (Ann. Min. [6], v. 453), in the mines of Cerro Blanco, near Copiapo, in long tin-white needles, intersecting copper-pyrites. Analysis gave 22·4 per cent. sulphur, 52·7 bismuth, 20·6 copper, and 4·1 iron (= 99·8).

TANNIC ACID. TANNIN. These terms are applied to certain substances occurring in the bark and other parts of plants, and distinguished by the following characters. They are mostly amorphous, have a slight acid reaction, and a rough but not sour taste; colour ferric salts black-blue or green; precipitate albumin and gelatin from their solutions; and unite with animal membrane into a mass which resists putrefaction, namely leather, the skin then becoming tanned. All these substances were formerly supposed to be identical with gallotannic acid (ii. 762), or to differ from it only in consequence of the admixture of foreign matters; but more exact investigation has shown that most of them differ in some essential properties from gallotannic acid, which indeed exists only in Turkish and Chinese gall-nuts, and in ordinary oak-apples. Of the other varieties of tannin, the most distinctly characterised are *caffetannic acid* (i. 709), *catechutannic* or *cachoutannic acid* (i. 817), *morintannic acid* or tannin of fustic (iii. 1049), *quercitannic acid* or tannin of oak-bark (v. 6), and *quinotannic* or *cinchona-tannic acid* (v. 30).

The tannins may be divided into two groups—those which give black or blue, and those which give olive-green precipitates with ferric salts; and Stenhouse has shown that most of the tannins which give bluish-black precipitates with ferric salts are glucosides, being resolved by boiling with dilute acids into glucose and another substance, a property first pointed out by Strecker in the case of gallotannic acid, which yields glucose and gallic acid:

$$C^{27}H^{22}O^{17} + 4H^2O = C^6H^{12}O^6 + 3C^7H^6O^5;$$

whereas, among those which give green precipitates with ferric salts, only one (namely, the tannin of willow-bark) appears to be a glucoside.

Gallotannic acid submitted to dry distillation yields pyrogallic and metagallic acids, together with carbonic anhydride (ii. 765):

$$\underset{\text{Gallotannic acid.}}{C^{27}H^{22}O^{17}} = \underset{\text{Pyrogallic acid.}}{3C^6H^6O^3} + \underset{\text{Metagallic acid.}}{C^6H^4O^2} + 3CO^2;$$

whereas all those tannins which turn ferric salts green, yield, by dry distillation, oxyphenic acid or pyrocatechin, $C^6H^6O^2$, which differs from pyrogallic acid by containing 1 at. oxygen less (iv. 315).

All tannins are remarkable for the avidity with which they absorb oxygen, especially in presence of alkalis, being thereby converted into bodies of various colour—red, brown, black, and even green: *e.g.*, gallotannic acid into tannoxylic or tannomelanic acid; caffetannic acid into viridic acid; quinotannic acid into cinchona-red, &c.

Tannins occur especially in perennial plants, but are likewise found in annuals and biennials. They occur in the perennial roots of herbaceous plants, in the bark of most tree-stems, and in the young branches of shrubs and other woody plants. They are also found in the husks of fruits and seeds, and in unripe fruits, less frequently in the leaves, and least of all in the petals. According to Wahlenberg, they are never found in the interior of the seed, or in poisonous plants, or in such as contain caoutchouc or milky juice.

Iron-blueing tannins are found in gall-nuts and oak-apples; in the leaves, bark, &c. of the oak, poplar, birch, hazel-nut, and other trees; the leaves of *Arbutus Uva-ursi*, *Arbutus Unedo*, and *Lythrum Salicaria*; the stalks of *Ribes rubrum*; the bark of *Cornus mascula*, and many other plants and vegetable organs. Iron-greening tannins occur in catechu, cinchona-barks, pines, and fir; in the root of *Crameria triandra*, *Rheum rhaponticum*, *Potentilla tormentilla*; in the bark of *Salix triandra* and *S. undulata*, of *Alnus glutinosa*, *Pinus Larix*, *Rhizophora Mangle* (the common black mangrove), and of many other plants.

R. Wagner (Bull. Soc. Chim. 1866, ii. 461) divides tannins into pathological tannins, found only in diseased vegetable tissues, such as gall-nuts and oak-apples; and physiological tannins, which occur in bark and other parts of plants in their ordinary state. Both kinds of tannins precipitate gelatin from its solution, but only the physiological tannins are capable of forming with it a true leather not liable to putrefy.

All varieties of tannin are precipitated by organic alkaloïds. According to Wagner, 1 gramme of quercitannic acid requires for precipitation 0·3715 grm. of cinchonine; and assuming that the tannins of sumach and other astringent substances form, with a solution of sulphate of cinchonine, precipitates having the same composition, he obtains the following results respecting the strength of various substances used in tanning:—

Bark of young oaks contains . .	10·80 per cent tannin.
Ordinary oak-bark	6·25 „
Pine-bark	7·33 „
Beech-bark	2·00 „

Sumach (first quality) contains	16·50	per cent. tannin.
„ (second quality)	13·00	„
Valonia (first quality)	26·75	„
„ (second quality)	19·00	„
Bablah	14·50	„
Grape-seeds freed from oil	6·50	„
Hops (harvest of 1865)	4·25	„

Schulzeff (Bull. Soc. Chim. 1866, ii. 465) has observed that the precipitation of tannin by gelatin is greatly facilitated by the addition of sal-ammoniac, and he has applied the reaction to facilitate the volumetric estimation of tannin. For this purpose he saturates a graduated solution of tannin with sal-ammoniac, and determines the number of cubic centimetres of a solution of gelatin required to precipitate a given quantity of the former. He then exhausts the substance to be analysed with boiling water, and adds to the extract the titrated solution of gelatin. The deposition of the precipitate may be still further facilitated by introducing into the vessel a small quantity of pounded glass or sharp sand.

TANNIGENAMIC ACID. Syn. with Gallamic Acid (ii. 759).

TANNINGENIC ACID. Syn. with Catechin (i. 816).

TANNOMELANIC ACID. $C^6H^4O^3$.—This acid, discovered by Büchner (Ann. Ch. Pharm. liii. 373), who however assigned to it the formula $C^{14}H^5O^8$, is produced by adding gallotannic acid to boiling potash-ley of specific gravity 1·27, as long as effervescence is thereby produced. The liquid is kept in a state of ebullition, till a sample mixed with acetic acid remains clear on cooling, then supersaturated with acetic acid, and evaporated to dryness over the water-bath; and the residue is treated with strong alcohol, which dissolves acetate and gallate of potassium. The residue is dissolved in water, and the solution is mixed with acetic acid and acetate of lead, which throws down tannomelanate of lead, in the form of a black-brown powder containing (according to Gerhardt) $3C^{12}H^6Pb''O^6.2Pb''H^2O^2$. Tannomelanic acid may be supposed to be formed either from gallic or from tannoxylic acid (*infra*):

$$\underset{\text{Gallic acid.}}{C^7H^6O^5} + O = \underset{\text{Tannomelanic acid.}}{C^6H^4O^3} + CO^2 + H^2O.$$

$$\underset{\text{Tannoxylic acid.}}{C^7H^6O^6} = \underset{\text{Tannomelanic acid.}}{C^6H^4O^3} + CO^2 + H^2O.$$

TANNOPIC ACID. $C^{28}H^{30}O^{14}$? (Rochleder and Kawalier, Wien. Akad. Ber. xxix. 22.)—A kind of tannin occurring in the needles of the Scotch fir, gathered about Easter. The alcoholic extract of the needles, evaporated after addition of water, yielded a watery liquid together with resin. The liquid was mixed with neutral acetate of lead; the clear filtrate completely precipitated with that salt; the washed precipitate drenched with dilute acetic acid; and the filtrate precipitated with basic acetate of lead. The resulting precipitate, suspended in water and decomposed by sulphydric acid, yielded a solution of tannopic acid, which was precipitated therefrom by sulphuric acid. This acid, in warm solution, oxidises readily in contact with the air; whether it is thereby converted into oxypinitannic acid (iv. 319), and whether the same conversion takes place in the living plant, has not been determined. The acid is decomposed by sulphuric or hydrochloric acid, yielding a red easily decomposible product.

TANNOXYLIC ACID. *Rufitannic Acid.*—An acid produced by the oxidation of gallic acid under the influence of alkalis. It was discovered by Büchner (Ann. Ch. Pharm. liii. 369), who assigned to it the formula $C^{15}H^5O^{11}$ or $C^{15}H^{10}O^{11}$, or, in the free state, perhaps $C^{15}H^6O^{12}$ or $C^{15}H^{12}O^{12}$. According to Gerhardt, its composition and formation are better represented by the formula $C^7H^6O^6$. To prepare it, a moderately strong solution of potash is saturated in the cold with tannic acid; and the solution, which soon turns red, is left to stand for some days till it becomes dark-red and nearly opaque. It is then precipitated with acetate of lead, the resulting brick-red precipitate is treated with hot acetic acid to dissolve undecomposed tannate of lead, and the tannoxylate of lead ($8C^7H^4Pb''O^6.3Pb''H^2O^2$, according to Gerhardt), which remains as a red precipitate, is decomposed by heating with alcohol and sulphuric acid. A dark-red solution of tannoxylic acid is thereby obtained, which on evaporation leaves the acid as a brown-red amorphous substance. It may be supposed to be formed from gallic acid by simple addition of oxygen: $C^7H^6O^5 + O = C^7H^6O^6$. (Gerhardt.)

TANSY. See Tanacetum Vulgare (p. 658).

TANTALITE. Native ferrous tantalate. See Tantalates (p. 666).

TANTALUM. *Atomic weight*, 182. *Symbol*, Ta. (Ekeberg, Crell's Annalen. 1803, Bd. i.—Berzelius, Pogg. Ann. iv. 6.—Wöhler, *ibid.* xlviii. 91.—H. Rose, *ibid.* lxiii. 317; lxix. 115; lxx. 157; lxxiv. 85, 285; xc. 456; xcix. 65; Jahresb. 1856, p. 366; 1857, p. 176.—Hermann, J. pr. Chem. lxv. 81; lxx. 193; Jahresb. 1857, p. 175; 1858, p. 149; Bull. Soc. Chim. 1866, ii. 22.—Blomstrand, Jahresb. 1865, p. 195; Bull. Soc. Chim. 1866, ii. 27.—Marignac, *ibid.* pp. 111, 118.)

This metal was discovered in 1802, by Ekeberg, in two Swedish minerals, tantalite and yttrotantalite. A very similar metal, columbium, had been discovered in the preceding year by Hatchett (Crell's Annalen. 1802, i. 197, 257, 352), in columbite from Massachusetts; and Wollaston, in 1807 (Gilb. Ann. xxxvii. 98), on comparing the compounds of these metals, concluded that they were identical, an opinion which was for many years received as correct; but their separate identity has been completely established by the researches of H. Rose (commenced in 1846), who gave to the metal obtained from the American and Bavarian columbites the name *Niobium* (iv. 48), by which it is now universally known. More recently, Marignac has shown that nearly all tantalites and columbites contain both tantalum and niobium or columbium; some tantalates from Kimito in Finland being, however, free from niobium, and some of the Greenland columbites containing only the latter metal unmixed with tantalum. In all these minerals, tantalum exists as a tantalate of iron and manganese; yttrotantalite is essentially a tantalate of yttrium, containing also uranium, calcium, iron, and other metals. Tantalum is also contained in some varieties of wolfram.

Metallic tantalum is obtained by heating the fluotantalate of potassium or sodium with metallic sodium in a well-covered iron crucible, and washing out the soluble salts with water. The reduced metal thus obtained is not quite pure, being more or less contaminated with acid tantalate of sodium, the quantity of which may, however, be diminished by covering the mixture in the crucible with chloride of potassium.

Tantalum is a black powder, which (according to H. Rose) is a good conductor of electricity, and, after ignition in a stream of hydrogen, has a specific gravity of 10·78. When heated in the air, it burns with a bright light, and is converted, though with difficulty, into tantalic oxide. It is not attacked by sulphuric, hydrochloric, nitric, or even nitromuriatic acid. It dissolves slowly in warm aqueous hydrofluoric acid, with evolution of hydrogen, and very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum in its principal compounds is pentatomic, the formula of tantalic chloride being $TaCl^5$, that of tantalic fluoride TaF^5, and that of tantalic oxide (which, in combination with bases, forms the tantalates) TaO^5. There is also a tantalous oxide having the composition TaO^2, and a corresponding sulphide, TaS^2.

TANTALUM, BROMIDE OF, probably $TaBr^5$.—Prepared, like the chloride, by passing bromine-vapour through a tube filled with a mixture of tantalic oxide and porous charcoal. It is usually coloured yellow by excess of bromine, from which it cannot easily be freed.

TANTALUM, CHLORIDE OF, or **TANTALIC CHLORIDE,** $TaCl^5$.—Tantalum is not attacked by chlorine at ordinary temperatures, but, when gently heated in a stream of the gas, it is converted, with incandescence, into tantalic chloride, which distils off.

The chloride is prepared by passing chlorine-gas over a heated mixture of tantalic oxide and charcoal. Tantalic oxide is mixed with starch or sugar, and the mixture completely charred by ignition in a covered crucible. It is then introduced in small pieces into a glass tube, which is strongly heated by a charcoal-fire, while a stream of dry carbonic anhydride is passed through it. As soon as all the moisture is expelled, the tube is left to cool, the flow of carbonic anhydride being still kept up; the carbonic anhydride apparatus is then replaced by a chlorine apparatus, and the tube again heated, after the carbonic anhydride and atmospheric air have been completely expelled by the chlorine. Chloride of tantalum is then obtained in the form of a sublimate having a pure yellow colour. If, however, the tantalic oxide contains tungstic oxide, the colour of the sublimate is red; and if stannic or titanic oxide is present, yellow drops of liquid chloride are also produced. (H. Rose and R. Weber, Ann. Ch. Pharm. lxxxviii. 246.)

Tantalic chloride begins to volatilise at 144°, and melts to a yellow liquid at 221°. Its vapour-density, at temperatures between 350° and 440°, is equal to 12·42 (Deville and Troost, Bull. Soc. Chim. 1866, ii. 120); agreeing very nearly with the density calculated from the formula $TaCl^5$, namely 12·46 ($= \frac{182 + 5 \,.\, 35{\cdot}5}{2} \times 0{\cdot}0693$).

Tantalic chloride is decomposed by *water*, yielding hydrochloric and tantalic acids, but the decomposition is not complete even at the boiling heat; water containing a small quantity of ammonia decomposes it, even at ordinary temperatures.—*Potash* decomposes it, but not completely; *carbonate of potassium* does not affect it, even at the boiling heat.—*Hydrochloric acid* dissolves tantalic chloride at ordinary temperatures, forming a turbid liquid, which gelatinises after a while; the jelly yields to cold water only traces of tantalic acid. Boiling hydrochloric acid dissolves tantalic chloride incompletely, and the liquid does not gelatinise.—Strong *sulphuric acid* dissolves the chloride, at ordinary or slightly elevated temperatures, with evolution of hydrochloric acid, forming an opaline liquid, which becomes very turbid at the boiling heat, and solidifies to an opaline jelly on cooling.—*Ammonia-gas* converts tantalic chloride, at a red heat, into nitride of tantalum. (H. Rose.)

TANTALUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions.*—Tantalic oxide, fused with *borax*, either in the outer or in the inner flame, forms a transparent glass, which however, if the quantity of tantalum is somewhat large, may be rendered opaque by interrupted blowing or flaming, but recovers its transparency by long exposure to the continued blast. A very large quantity of tantalic oxide renders the glass opaque.—With *microcosmic salt* it forms, in either flame, a clear colourless glass, which does not turn red on addition of a ferrous salt.—With *sodic carbonate* it produces effervescence, but does not fuse into a bead or undergo reduction.

2. *Reactions in Solution.*—The tantalates of the alkali-metals are soluble in water (p. 666).—*Hydrochloric acid*, added in excess to the solutions, first precipitates tantalic acid, and then redissolves it, forming a slightly opalescent liquid.—*Sulphuric acid* also precipitates the tantalic acid, but does not redissolve it when added in excess.—*Carbonic acid gas*, passed through the solution of an alkaline tantalate, precipitates the whole of the tantalic acid in the form of an acid salt.—*Chloride* or *sulphate of ammonium* also precipitates the tantalic acid from these solutions, in the form of hydrate mixed with small quantities of ammonia and the fixed alkali. The presence of carbonate of potassium or sodium prevents the formation of this precipitate at ordinary temperatures; but it then appears after boiling for some time. Sulphide of ammonium produces no precipitate.—*Chloride of barium* or *calcium* forms a precipitate of tantalate of barium or calcium, insoluble in water and in ammoniacal salts.—*Nitrate of silver* forms, in the solution of a neutral alkaline tantalate, a white precipitate, which is turned brown by a small quantity of ammonia, and dissolves in a larger quantity. A solution of *basic mercurous nitrate* forms a yellowish-white precipitate, which turns black when heated.—*Ferrocyanide of potassium*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate; *ferricyanide of potassium* a white precipitate.—*Infusion of galls*, added to a solution of an alkaline tantalate acidulated with sulphuric or hydrochloric acid, forms a light-yellow precipitate, soluble in alkalis.—*Zinc*, immersed in the solution of an alkaline tantalate acidulated with hydrochloric acid, does not produce any blue colour; neither is that colour produced, or but very faintly, on addition of sulphuric acid. But if chloride of tantalum be dissolved in strong sulphuric acid, and then water and metallic zinc added, a fine blue colour is produced, which does not change to brown, but soon disappears. The blue colour is also produced on placing zinc in a solution of tantalic chloride in hydrochloric acid to which a small quantity of water has been added; too much water, however, prevents its formation.

These characters are sufficient to distinguish tantalum from all other metals. From niobium, which it most resembles, it is distinguished by the behaviour of tantalic oxide before the blowpipe, especially with microcosmic salt; (2), by the reactions of the soluble tantalates with hydrochloric acid, sal-ammoniac, ferrocyanide and ferricyanide of potassium, and infusion of galls.[*]—From titanium it is distinguished by the behaviour of the oxides before the blowpipe; by the perfect insolubility of tantalic oxide in strong sulphuric acid after ignition; and by the fact that when tantalic oxide is fused with acid sulphate of potassium, and the mass treated with cold water, the tantalic oxide remains undissolved in combination with sulphuric acid, whereas titanic oxide similarly treated yields a fused mass, which dissolves completely in a considerable quantity of cold water, provided the fusion has been sufficiently prolonged.—From silica, tantalic oxide is distinguished by its behaviour before the blowpipe, silica being insoluble in microcosmic salt, and fusing to a transparent bead when heated on charcoal with a small quantity of sodic carbonate. The behaviour of tantalic oxide with zinc, with tincture of galls, and with hydrofluoric acid, also distinguishes it from silica.

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[*] See vol. iv. pp. 50, 51.—The niobous oxide and niobites there mentioned are the compounds now called niobic oxide and niobates, Marignac having shown that there is only one oxide of niobium, and that Rose's niobic acid was a mixture of niobic and tantalic acids (iv. 785).

3. *Estimation and Separation.*—Tantalum is estimated in the form of tantalic oxide, Ta^2O^5, containing 81·98 per cent. of the metal. Tantalic oxide or anhydride may be separated from the bases with which it occurs in nature—namely, lime, magnesia, yttria, zirconia, and the oxides of iron, manganese, and uranium—by fusion with *hydrate* or, better, with *acid sulphate of potassium*, in the manner to be presently described (p. 665). Some tantalates may be decomposed by *sulphuric acid*, the tantalic acid being separated in the insoluble state, and all the bases passing into solution. Tantalate of zirconium may be decomposed in this manner. On treating that compound with strong sulphuric acid, and digesting the cooled mass for some time with a large quantity of water, sulphate of zirconium dissolves, and tantalic oxide remains in combination with sulphuric acid, from which it may be purified by repeated boiling with water.

From the alkalis, tantalic acid may be completely separated by sulphuric acid, provided the compound is soluble in water. In the contrary case, it must first be fused with carbonate or hydrate of potassium. If, however, the quantity of alkali is to be likewise estimated, the compound must be rendered soluble by fusion with sulphate of ammonium. (H. Rose.)

From titanium, with which it sometimes occurs in nature, tantalum may be separated by fusing the mineral with acid sulphate of potassium, and treating the fused mass with a large quantity of water. Titanic acid then dissolves, especially if the water is slightly acidulated with hydrochloric acid, while tantalic sulphate remains undissolved. The titanic acid is precipitated from the solution by boiling: the separation is, however, not very complete. In some cases the decomposition may be effected by sulphuric acid.

The separation of tantalum from niobium is effected by means of *acid fluoride of potassium*, whereby the former metal is converted into fluotantalate of potassium, $2KF.TaF^5$, requiring 151 to 157 pts. of water acidulated with hydrofluoric acid to dissolve it at ordinary temperatures, and the latter into fluoxyniobate of potassium, $2KF.NbOF^3.H^2O$, soluble in 12·4 to 13 pts. of cold water. The mineral (a tantalite or columbite) having been decomposed by fusion with three times its weight of acid potassic sulphate, the collective weight of the niobic and tantalic oxides thereby separated is ascertained; they are then again fused with acid sulphate of potassium; the sulphate is dissolved out by water; the residue is treated with hydrofluoric acid; and a boiling solution of hydropotassic fluoride is gradually added. The liquid thus obtained yields, after a certain degree of concentration, a deposit of potassic fluotantalate, which must be washed with water on a weighed filter, till the wash-waters no longer yield an orange-coloured precipitate with infusion of galls.

4. *Atomic Weight of Tantalum.*—The older experiments on the constitution of the tantalum-compounds did not yield correct results, because the tantalum used was impure, containing niobium. Berzelius regarded tantalic oxide as Ta^2O^3; H. Rose regarded it as TaO^2, the chloride as $TaCl^4$, &c. But from the observations of Marignac on the isomorphism of the fluotantalates and fluoniobates, and from the vapour-density of the chloride (p. 662), it appears that tantalum is pentatomic, forming the compounds $TaCl^5$, TaF^5, Ta^2O^5, &c.

Marignac has determined the atomic weight of tantalum chiefly from the composition of the fluotantalates of potassium and ammonium, which are anhydrous and do not undergo any alteration at 100°. The potassium-salt was treated with pure concentrated sulphuric acid; the excess of that acid gradually driven off, the temperature being finally raised to 400°; and the residue was boiled with water, which dissolved the acid sulphate of potassium, and left tantalic sulphate in small granular crystals, which, when calcined at a strong heat, yielded pure tantalic oxide. The acid sulphate of potassium was reduced, by evaporation and calcination, to neutral sulphate, which was weighed. Four closely accordant analyses yielded, as a mean result, 56·6 pts. tantalic oxide to 45·4 pts. neutral sulphate of potassium, according to which the atomic weight of tantalic oxide, Ta^2O^5, = 414·6, and that of tantalum = 182·3.

By calculating merely from the weight of the neutral sulphate of potassium compared with the original weight of the fluotantalate, $2KF.TaF^5$, the atomic weight of that salt is found to be 392·8, whence Ta = 181·8, a number very near the preceding.

Fluotantalate of ammonium, by conversion into tantalic oxide, loses 36·75 per cent. of its weight, a loss corresponding to the replacement of $2NH^4 + 7F = 169$ by $\frac{5}{2}O = 40$, leaving a difference of 129; and the proportion, $36{\cdot}75 : 100 = 129 : x$, gives $x = 351$ for the atomic weight of fluotantalate of ammonium, whence Ta = 182. This is the number adopted by Marignac for the atomic weight of tantalum;[*] it agrees perfectly with the vapour-density of the chloride (p. 662).

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[*] H. Rose (Ann. Ch. Pharm. c. 126) found in impure chloride of tantalum 49·25 per cent. tantalum and 50·75 chlorine, which, for the formula $TaCl^5$, gives Ta = 172.

TANTALUM, FLUORIDE OF. TaF^5.—Ignited tantalic oxide does not dissolve in aqueous hydrofluoric acid, but the hydrate dissolves, forming a clear solution, which, when evaporated, partly gives off the tantalum as fluoride, but likewise leaves a residue of oxyfluoride. (H. Rose.)

Fluotantalates, $2MF.TaF^5 = M^2TaF^7$.—The solution of tantalic fluoride mixed with alkaline fluorides forms soluble and crystallisable double salts, partially studied by Berzelius and H. Rose, more completely by Marignac. There do not appear to be any fluoxytantalates corresponding to the fluoxyniobates (iv. 786), unless the insoluble compounds which tend to form when the fluotantalates are dissolved in water, can be considered as such; but these compounds do not crystallise, and do not appear to possess a constant composition. (Marignac.)

Fluotantalate of Ammonium, $(NH^4)^2TaF^7$, is anhydrous, very soluble in water, and crystallises in thin plates with bevelled edges.

The *potassium-salt*, K^2TaF^7, crystallises in monoclinic prisms isomorphous with the fluoniobate. It is more soluble in hot than in cold water. By prolonged boiling with water, it changes into an insoluble salt, the composition of which is nearly that represented by the formula $Ta^2O^5.2K^2TaF^7$. The formation of this insoluble compound affords the means of detecting the smallest quantity of fluotantalate in a solution of fluoxyniobate of potassium. (Marignac.)

The *sodium-salt*, $Na^2TaF^7.H^2O$, forms monoclinic prisms, which give off their water of crystallisation at 100°.

The *cupric salt*, $Cu''Ta^2F^7.4H^2O = Cu''F^2.Ta^2F^5.4H^2O$, prepared by adding cupric oxide to a solution of tantalic oxide in hydrofluoric acid, forms beautiful blue, transparent, rhomboïdal prisms with four-sided summits. It is deliquescent, and very soluble in water.

The *zinc-salt*, $Zn''Ta^2F^7.7H^2O = ZnF^2.TaF^2.7H^2O$, prepared like the copper-salt, is too deliquescent to admit of complete purification, so that its formula must be regarded as only approximate. (Marignac.)

TANTALUM, NITRIDE OF. Obtained by the action of ammonia-gas on chloride of tantalum, at a heat gradually raised to redness; or less pure by heating tantalic oxide in ammonia-gas. It is a black microcrystalline powder, which acquires metallic lustre by burnishing, and conducts electricity; when fused with hydrate of potassium, it gives off ammonia-gas. It is not attacked by nitric acid, or by a mixture of that acid with hydrochloric or hydrofluoric acid. (H. Rose, Ann. Ch. Pharm. c. 146).

TANTALUM, OXIDES OF. Tantalum forms two oxides, a dioxide and a pentoxide, the latter uniting with bases, and forming the tantalates.

Dioxide of Tantalum, or **Tantalous Oxide,** TaO^2.—This oxide is produced by exposing tantalic oxide in a brasqued crucible to the strongest heat of a blast-furnace, a thin film on the outside being at the same time reduced to the state of metal. It is a dark-grey mass, which scratches glass, and acquires metallic lustre by burnishing (Berzelius). When heated to redness, in contact with the air, it takes up 4 per cent. of oxygen, and is converted into tantalic oxide. By calculation, TaO^2 requires 3·74 per cent. of oxygen to convert it into Ta^2O^5. (Marignac.)

Pentoxide of Tantalum, Tantalic Oxide or **Anhydride,** Ta^2O^5. In the hydrated state, **Tantalic Acid.**—This oxide is formed when tantalum burns in the air, also by the action of water on tantalic chloride, and may be separated as a hydrate from the tantalates by the action of acids. It is usually prepared from tantalite, which is a tantalate of iron and manganese, containing small quantities of stannic and tungstic acids, and a varying (sometimes considerable) quantity of niobic acid, by fusing the pulverised and levigated mineral with twice its weight of potassic hydrate; or, better, with excess of acid potassic sulphite (6 or 8 pts. according to Berzelius, 3 pts. according to Marignac), in a platinum crucible.

The mass, when cold, is pulverised and repeatedly boiled with fresh quantities of water, till no more sulphate of potassium, iron, or manganese is dissolved out of it; and the residue, consisting of tantalic acid mixed with ferric oxide, stannic acid, tungstic acid, and niobic acid, is then digested with sulphide of ammonium containing excess of sulphur, which removes the tin and tungsten as sulphides, and converts the iron into insoluble sulphide. The liquid is filtered, and the tantalic acid is washed with water containing sulphide of ammonium, then boiled with strong hydrochloric acid to remove the iron, and washed with boiling water. It may still, however, contain silicic and niobic acids. To remove the former, it is dissolved in aqueous hydrofluoric acid, the filtered solution mixed with sulphuric acid and evaporated to dryness, and the residue ignited as long as its weight continues to diminish (Berzelius; H. Rose). To remove the niobium, the tantalic acid is redissolved in aqueous hydrofluoric acid, and treated with acid fluoride of potassium in the manner already described (p. 664). The pure fluotantalate of potassium thus obtained is decomposed by heating with sulphuric acid; the sulphate of potassium dissolved out by boiling with water; and the remaining tantalic sulphate strongly ignited to expel the sulphuric acid (**Marignac**). By this process, Marignac has prepared considerable quantities of tantalic oxide from columbites containing that compound together with niobic oxide.

Anhydrous tantalic oxide, obtained by igniting the hydrate or sulphate, is a white powder, which remains white when heated, or acquires but a very faint tinge of yellow. Its specific gravity varies from 7·022 to 8·264, increasing with the temperature to which it has been exposed (**H. Rose**); according to **Marignac**, the specific gravity = 7·60 to 7·64. **Nordenskjöld** and **Chydenius** (Pogg. Ann. cx. 642; Jahresb. 1860, p. 145), by fusing it with microcosmic salt, and treating the fused mass with hydrochloric acid, obtained, together with the amorphous oxide, a small quantity of heavy needle-shaped crystals, which were rhombic combinations with the dominant faces, ∞P, $\bar{P}\infty$, and the angles $\infty P : \infty P = 100° 42'$; $\bar{P}\infty : \bar{P}\infty$ over the principal axis $= 90° 20'$. Tantalic oxide neither melts nor volatilises when heated, and is destitute of taste and smell. It is reduced to the metallic state in the circuit of a very powerful voltaic battery; partially also by very strong ignition in contact with *charcoal*. When heated in *ammonia-gas*, it yields nitride of tantalum; and by ignition in *cyanogen-gas*, it is partially converted into nitride and cyanide of tantalum (**H. Rose**). Ignited in vapour of *carbonic disulphide*, it yields disulphide of tantalum:

$$Ta^2O^5 + 5CS^2 = 2TaS^2 + 5CO + S^6.$$

Tantalic oxide is insoluble in all acids, and can only be rendered soluble by fusion with hydrate or carbonate of potassium.

Hydrated tantalic oxide, or *Tantalic acid*, obtained by precipitating an aqueous solution of potassic tantalate with hydrochloric acid, or by decomposing tantalic chloride with water containing a little ammonia, is a snow-white bulky powder, which reddens litmus-powder while moist, and dissolves in hydrochloric and hydrofluoric acids. When strongly heated, it gives off its water and becomes incandescent. The hydrate, obtained by fusing tantalite with acid sulphate of potassium as above described, is of a denser and more crystalline character, insoluble in all acids except hydrofluoric and strong sulphuric acids, and is precipitated from the sulphuric solution by water. When heated it becomes anhydrous, but does not emit light.

Tantalates, $\left.\begin{matrix}M^2O\\ \text{or } M''O\end{matrix}\right\}Ta^2O^5$ and $4M^2O.3Ta^2O^5$ * (according to **Marignac**).—The first of these formulæ includes the native tantalates; the second, certain easily crystallisable tantalates of the alkali-metals.

The tantalates of the *alkali-metals* are soluble in water, and are obtained by fusing tantalic oxide with caustic alkalis. Tantalic oxide fused with *hydrate of potassium* in a silver crucible, forms a transparent mass of potassic tantalate, which, after cooling, dissolves completely in water. With *hydrate of sodium*, it fuses into an opaque turbid mass, and ultimately deposits a sediment, which is not taken up by fusion with any excess of the alkali. Water poured upon the fused mass when cold, dissolves out the excess of soda, but not a trace of tantalic acid; and the residue, when treated with fresh water, dissolves and forms an opalescent solution of acid sodic tantalate, which salt is completely insoluble in a strong solution of caustic soda, and is therefore precipitated on mixing the liquid with the solution of soda previously obtained by treating the fused mass with water. When tantalic oxide is fused with *potassic or sodic carbonate*, the fused mass is not completely soluble in water.

The tantalates of the *earth-metals* and *heavy metals* are insoluble in water, and are formed by precipitation (p. 663).

Ferrous Tantalate, $FeO.Ta^2O^5$.—This salt occurs native as **tantalite** and **tapiolite**, rarely however quite pure, the iron being generally more or less replaced by manganese, and the tantalum by niobium, tin, and zirconium. Columbite or niobite is a mineral of analogous constitution, containing both tantalum and niobium, the latter however predominating: some of the Greenland columbites contain only niobium, without tantalum.

Tantalite is found at several localities in Finland, at Broddbo and Finbo near Fahlun in Sweden, and at Chanteloub near Limoges in France. It occurs in trimetric crystals having the axes $a : b : c = 0·6517 : 0·8170 : 1$, and usually bounded by the faces P and $\infty\breve{P}\frac{4}{3}$, with $\infty\breve{P}\infty$, $\infty\bar{P}\infty$, $\breve{P}\frac{3}{2}$, $\breve{P}\frac{1}{2}$, $\breve{P}\infty$, and $3\breve{P}\infty$ subordinate. Angle $P : P$ (terminal) $= 126° 1'$ and $112° 32'$; (lateral) $= 91° 44'$. Twins united by the face $\infty\breve{P}\infty$ are of frequent occurrence (**A. E. Nordenskjöld**, Pogg. Ann. ci.

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* According to H. Rose, the formula of the normal tantalates is $M^2O.2TaO^2$, which, with the pentatomic value of tantalum, becomes $5M^2O.4Ta^2O^5$. Several acid tantalates are described by **Rose** and by **Hermann**, for which see *Handw. d. Chem.* viii. 507.

625; Jahresb. 1857, p. 682). The mineral likewise occurs massive, and imbedded, in angular fragments of irregular shape. Hardness = 6·0 to 6·5. Specific gravity = about 7·0 to 8·0. Opaque, with imperfect metallic lustre and iron-black colour, black-brown to cinnamon-brown when pulverised. Fracture mostly uneven.

Nordenskjöld distinguishes as **ixiolite**, a stanniferous and manganiferous variety of tantalite, occurring, together with the preceding (which he designates as **skogbölite**, or simply as tantalite), at Skogböle in Finland. It likewise forms trimetric prisms, but having the axes $a : b : c$ = 0·5508 : 1·2460 : 1, and exhibiting the dominant combination $oP . \infty\bar{P}\infty . \infty\breve{P}\infty$, with P, ∞P; $\breve{P}\infty$, $3\breve{P}\infty$, and $\frac{1}{3}\bar{P}\infty$ subordinate. Hardness = 6·0 to 6·5. Specific gravity = 7·0 to 7·1. Lustre faintly metallic. Colour black-grey to steel-grey, brown in powder. Fracture flat, conchoïdal, sometimes nearly uneven.

The more stanniferous varieties of tantalite are designated by Hausmann (*Lehrb. d. Mineral.* p. 960) as **Cassiterotantalite**, the less stanniferous as **Siderotantalite**; the former are also sometimes designated, according to their localities, as **Finbo** and **Broddbo tantalites**, the latter as **Kimito** and **Tammela tantalites**.

Tapiolite, occurring at Sukkula in Tammela, Finland, has the composition of tantalite, but crystallises in dimetric forms, having the same angles and ratio of axes as rutile; ferrous tantalate is therefore dimorphous (or trimorphous, if ixiolite is really a distinct crystallographic species). (Nordenskjöld, Pogg. Ann. cxxii. 604; Jahresb. 1864, p. 855.)

All tantalites (including tapiolite) are infusible and unalterable before the blowpipe. They dissolve easily in borax and microcosmic salt, giving the reactions of iron and manganese. The more stanniferous varieties, heated on charcoal with sodic carbonate, yield numerous spangles of tin. Tantalites are not attacked by acids.

The following analyses of tantalite are from Rammelsberg's *Mineralchemie*, pp. 390, 391; those of tapiolite are by Arppe (Jahresb. 1862, p. 753) and A. Nordenskjöld (Pogg. Ann. cxxii. 604; Jahresb. 1864, p. 856):—

Chanteloub, near Limoges.

	Damour.	Jeuzsch.		Chandler.
Specific gravity	7·64—7·65	7·703	7·027—7·042	7·533
Tantalic oxide	82·98	83·55	78·98	79·89
Stannic oxide	1·21	1·02	2·36	1·51
Silica	0·42			
Zirconia	. .	1·54	5·72	1·32
Ferrous oxide	14·62	14·48	13·62	14·14
Manganous oxide	trace	trace	trace	1·82
	99·23	100·59	100·68	98·68

Torroby in Tammela, Finland.

	Nodenskjöld.	Jacobson.	Brooks.	Weber.
Specific gravity	7·264	7·197	. .	7·414
Tantalic oxide	83·49	84·15	84·70	83·90
Stannic oxide	trace	0·32	0·50	0·66
Ferrous oxide	13·75	14·68	14·29	13·81
Manganous oxide	1·12	0·90	1·78	0·74
Lime	. .	0·07		
Cupric oxide	. .	1·81	0·04	0·11
	98·36	101·93	101·31	99·22

Skogböle in Kimito, Finland.

	Klaproth.	Berzelius.		Hermann.	Nordenskjöld.	Warnum.	Weber.	
Specific gravity	.	.	7·936	.	7·85	7·112—7·155	.	7·277
Tantalic oxide	88	83·2	85·85	84·09*	84·44	77·83	75·71	76·81
Stannic oxide	.	0·6	0·80	0·70	1·26	6·81	9·67	9·14
Ferric oxide	.	.	. .	10·08				
Ferrous oxide	10	7·2	12·94	3·33	13·41	8·47	9·80	9·49
Manganous oxide	2	7·4	1·60	1·32	0·96	4·88	4·32	4·27
Lime	.	. .	0·56	. .	0·15	0·50	. .	0·41
Cupric oxide	.	. .	0·72†	. .	0·14	0·24	. .	0·07
	100	98·4	102·47	99·52	100·36	98·73	99·50	100·19

* Silica.

† 73·07 Ta^2O^5 + 11·02 Nb^2O^5.

Fahlun, in Sweden.

	Nordenskjöld.	Berzelius.		
		Broddbo.		Finbo.
Tantalic oxide . .	83·79	68·22	66·34	66·99
Stannic oxide . .	1·78	8·26	8·40	16·75
Tungstic oxide . .	. .	6·19	6·12	
Ferric oxide . .	. .	9·58	11·07	7·67
Ferrous oxide . .	13·42			
Manganic oxide . .	. .	7·15	6·60	7·98
Manganous oxide .	1·63			
Lime . . .	. .	1·19	1·50	2·40
	100·62	100·59	100·03	101·79

Tapiolite, from Sukkula, Finland.

	Arppe.	Arppe.	A. Nordenskjöld.
Tantalic oxide . . .	83·66	82·71	83·06
Stannic oxide . . .	. .	0·83	1·07
Ferrous oxide . . .	15·44	15·99	15·78
	99·10	99·53	99·91

Marignac found in a Swedish tantalite:

Ta^2O^5	Nb^2O^5	SnO^2	FeO	MnO	
65·60	10·88	8·10	8·95	6·61	= 100·14.

He has also determined the quantity of tantalic oxide in various columbites, and concludes that if a perfect separation of the tantalic and niobic oxides could be effected, the specific gravity of this mineral would be found to increase proportionally to the percentage of tantalic oxide present. The following are the numbers obtained:—

	Sp.gr.	Ta^2O^5 p.c.
Columbite from Greenland	5·36	3·3
„ „ Acworth (New Hampshire) .	5·65	12·8
„ „ La Vilate (near Limoges) .	5·70	13·8
„ „ Bodenmais (Bavaria) . . .	5·74	13·4
„ „ Haddam (Connecticut) . .	5·85	10·0
„ „ Bodenmais	5·92	27·1
„ „ Haddam	6·05	30·4
„ „ Bodenmais	6·06	35·4
„ „ Haddam	6·13	31·5
Tantalite	7·03	65·6

Tantalite and columbite may be represented by the general formula (FeO; MnO)(Ta^2O^5; Nb^2O^5). Pure tantalite, as that of Kimito, contains from 83 to 85·8 per cent. tantalic oxide, and pure columbite or niobite, from Greenland, contains 76 to 78 per cent. niobic oxide; the other varieties yield intermediate numbers. (**Marignac.**)

Tantalate of Yttrium, or *Yttrotantalite*, is found native at Ytterby, in Sweden, in red felspar, and at Broddbo and Finbo near Fahlun, imbedded in quartz and albite. It exhibits the following varieties:—*a.* The black variety exhibits indistinct traces of crystallisation, in four- or six-sided irregular prisms and plates. Hardness = 5·5. Specific gravity = 5·395 (**Berzelius**), 5·67 (**Rose**), and 6·40 after heating. Lustre submetallic. Streak grey. Opaque.—*β.* The yellow variety is non-crystalline, and occurs in laminæ in the fissures of felspar. Hardness = 5. Specific gravity = 5·882 (**Ekeberg**); 5·810 (**Potyka**). Lustre resinous on the surface, vitreous on the fracture. Colour yellowish-brown to greenish. Streak white. Opaque.—*γ.* The brown variety occurs with the yellow in thin plates, or rarely in grains, presenting no trace of crystallisation. Hardness = 4·5 to 5. Lustre vitreous inclining to resinous. Colour black, with a very light shade of brown; slightly yellow in thin plates by transmitted light. Streak white.

The several varieties of yttrotantalite give off, when heated, from 3·9 to 5·54 per cent. water, are infusible alone before the blowpipe, but decrepitate, and assume a lighter colour. The black variety froths and fuses with carbonate of sodium. They dissolve in borax, but are not acted upon by acids.

The following analyses are taken from Rammelsberg's *Mineralchemie*, pp. 399, 400:—*a.* Black: lost by ignition 5·74 per cent. water (**Berzelius**).—*b.* Brown-black: those specimens which retained their colour on ignition lost 2·72 per cent. water; those which became yellowish, lost 6·06 per cent. (**Berzelius**).—*c.* Yellow:

lost by ignition 4·85 per cent. water (Berzelius).—*d.* Black: specific gravity = 5·67: lost by ignition 3·9 to 4·6 to 5·54 per cent., turning yellowish-brown, and acquired a specific gravity of 6·4 (Peretz).—*e.* Specific gravity 5·458 (Chandler).—*f.* *Yellow*, turning yellowish-brown before the blowpipe; partially decomposible by sulphuric acid. Specific gravity = 5·810 (Potyka):

	a.	*b.*	*c.*		*d.*	*e.*	*f.*
Tantalic oxide	57·00	51·81	59·50	60·12	55·80	57·27	55·60
Tungstic oxide	8·25	2·59	1·25	1·04	0·57	1·85	0·49
Stannic oxide	. .	. .	. .	. .	. .	0·10	0·10
Yttria	20·25	38·52	29·90	29·78	20·22	18·64	25·52
Cerous oxide	. .	. .	. .	. .	. .	. .	1·85
Uranic oxide	0·50	1·11	3·23	6·62			
Uranous oxide	. .	. .	. .	. .	3·75	5·10	7·00
Lime	6·25	3·26	3·29	0·50	7·18	4·78	3·60
Magnesia	. .	. .	. .	. .	1·33	0·75	0·19
Ferric oxide	3·50	0·56	2·72	1·15			
Ferrous oxide	. .	. .	. .	. .	5·96	4·82	0·77
Cupric oxide	. .	. .	. .	. .	0·40	0·69	0·43
Water	. .	. .	. .	. .	4·86	6·00	4·11
	95·75	97·85	99·89	99·21	100·07	100·00	99·66

The later analyses (*d*, *e*, *f*) may be represented, approximately, by the formula $2YO.TaO^2$ (Ta = 137) or $5YO.Ta^2O^3$ (Ta = 182). As, however, the mineral contains tungsten in varying proportion, the brown varieties apparently containing more than the yellow, the composition cannot be regarded as definitely established, especially as the formula just given takes no account of the water.

TANTALUM, SULPHIDE OF, TaS^2?, is obtained by igniting tantalic oxide in vapour of carbonic disulphide (p. 666), or by exposing tantalic chloride to the action of sulphydric acid gas: the product is not perfectly definite in either case. The first process yields a product containing 28·5 per cent., the second 24·08 per cent. sulphur: the formula above given requires 26·01 per cent. Sulphide of tantalum is a black substance, which acquires a brass-yellow colour by trituration in an agate mortar. Heated in an atmosphere of chlorine-gas, it is converted into tantalic chloride and chloride of sulphur. (H. Rose.)

TAPANHOACANGA. *Iron Conglomerate.*—A peculiar conglomerate occurring near Villa Rica, Itabira, Congonhas da Campo, Marianna, and other places in the province of Minas Geraes, Brazil, superposed on ferruginous mica-slate, clay-slate, itacolumite, and talcose slate, and consisting for the most part of angular fragments of iron-glance, ferruginous mica-slate, magnetic iron-ore, and brown hæmatite, bound together by an argillaceous cement, consisting of yellow, brown, or red ochre. The proportion of cement varies, and the mass contains, besides the minerals above mentioned, fragments of itacolumite, clay-slate, quarzite, and other rocks. The conglomerate often contains imbedded laminæ of gold. (*Handw. d. Chem.* viii. 512.)

TAPIOCA. A kind of starch obtained from the roots of *Janipha Manihot* (p. 408).

TAPIOLITE. The quadratic variety of ferrous tantalate found at Sukkula in Finland (p. 667).

TAR. *Theer. Goudron.*—A brown-black, viscid, oily liquid, produced, together with gaseous and watery products, in the dry distillation of organic bodies and bituminous minerals (ii. 339). It has generally an unpleasant, and sometimes a highly fetid odour; and is a mixture of various substances, acid, neutral, and alkaline, varying in composition according to the nature of the original body and the temperature applied in the distillation. Tar obtained from vegetable substances has an acid reaction, but coal-tar and the tar of animal substances are alkaline.

The principal groups of compounds contained in tars are liquid and solid hydrocarbons, alcohols, ethers, acids, and bases, together with resins, and empyreumatic products of indeterminate composition. On subjecting the tar to repeated distillation, the more volatile and liquid hydrocarbons, together with the alcohols and ethers, pass over first, while the less volatile oils consist chiefly of acid and basic compounds, and the last portions which distil over contain the solid hydrocarbons. The residue left after about half the tar has distilled over—called pitch, and likewise asphalt, when obtained from coal-tar—also contains solid hydrocarbons, together with resinous compounds.

By fractional distillation, the more volatile constituents of the tar are separated into portions of constant boiling-point, or boiling at temperatures comprised within narrow limits. The oily portions are treated with dilute acids, or (as Hofmann recommends) with hydrochloric acid gas, to remove the basic constituents. The several alkalis are then separated one from the other by fractional distillation, or by fractional precipitation of their platinum-salts (see PICOLINE, iv. 637). The oils freed from these bases are heated with strong sulphuric acid, which decomposes a number of indeterminate ampyreumatic products, whereby the subsequent separation of the remaining constituents is much facilitated.—The acid products contained in the several distillates are removed by means of alkalis. Strong potash-ley forms, with creosote and phenol, crystallised compounds, by means of which these bodies can be separated from the rest (iv. 389). Potash-ley and milk of lime are also frequently used to free the neutral oils from resinous bodies.—The separation of the neutral oily hydrocarbons one from the other is effected partly by fractional distillation, partly by other methods. Mansfield, by subjecting the portion of light coal-tar oil boiling between 80° and 90°, to a cold of − 10°, separated benzene in the crystalline form from the other hydrocarbons contained in it (i. 542). The olefines C^nH^{2n} may often be conveniently separated from other hydrocarbons by combining them with bromine (iii. 187); and by treating the bromine-compounds with sodium, the olefines may be set free, and separated one from another by fractional distillation. The hydrocarbons of the benzene-series, C^nH^{2n-6}, may be separated from mixtures of hydrocarbons by converting them into nitro-compounds.

The chief liquid constituents of wood-tar are methylic acetate, acetone, hydrocarbons—namely toluene, xylene, and cumene—methol (a mixture of volatile oils boiling between 100° and 265°), eupione, creosote, and a number of indefinite oxidised compounds, including picamar and capnomor. Amongst the solid portions are resinous matters more or less resembling colophony; also paraffin, naphthalene ($C^{10}H^8$), anthracene ($C^{14}H^{10}$), chrysene ($C^{18}H^{12}$), retene ($C^{18}H^{18}$), pyroxanthin, pittacal, and cedriret.

The more volatile portion of coal-tar, called *light-oil* or *coal-naphtha*, consists mainly of benzene and its homologues, together with a number of bases, $C^nH^{2n-5}N$, commencing with pyridine, C^5H^5N; the naphtha from cannel and Boghead coal is chiefly composed of alcoholic hydrides, homologous with marsh-gas, together with olefines and homologues of benzene. The less volatile oil, or *dead-oil* of coal-tar, contains phenol and cresol; also aniline, picoline, chinoline, and other volatile bases, and a number of solid hydrocarbons, including naphthalene, anthracene, chrysene, &c.—The tars obtained from peat and lignite are intermediate in composition between wood-tar and coal-tar. Shale-tar contains the same hydrocarbons as Boghead naphtha; also phenol, and a large quantity of the bases, $C^nH^{2n-5}N$, homologous with pyridine. (See NAPHTHA, iv. 2.)

The preparation of tar from coal, peat, lignite, and bituminous shale, has acquired great importance of late years, for obtaining paraffin and paraffin-oils for illumination and lubrication (iv. 342). Coal-tar has also acquired great value as the source of aniline-colours, and of phenol, picric acid, &c. Heavy coal-oil or dead-oil is remarkable for its antiseptic qualities, and is commonly used, without further purification, for the preservation of timber for railway sleepers, &c. It is also consumed as a fuel in common lamps, but is chiefly used for burning into lampblack.

Wood-tar likewise possesses powerful antiseptic properties, due to the creosote which it contains: hence it is also much used for the preservation of wood, especially in shipbuilding. In Russia and Sweden it is prepared, by a rude kind of distillation, from the resinous wood of the pine. A conical cavity is formed in the side of a hillock, the apex of the cone being below, and terminating in an aperture which opens into a trough leading to a reservoir for the tar. The kiln is filled with wood and partially covered over with turf; the pile is lighted at the top, and the combustion is regulated by covering it more or less completely with turf. The wood is thus charred from above downward, and the tar flows out at the bottom, charged with a considerable quantity of resin, and mixed with acetic acid and oil of turpentine. On heating, an impure essence of turpentine is distilled, leaving a black resinous substance, which constitutes ordinary pitch. The tar thus prepared is known in commerce as *Stockholm tar*.

The process just described is evidently a very wasteful one, especially entailing the loss of the greater part of the more volatile products of the distillation—acetic acid, wood-spirit, &c. Accordingly, wood-tar is now more generally prepared, like the other kinds of tar, by distillation in cylinders. (For details, see *Handw. d. Chem.*, viii. 650.)

TARAXACIN. See the next article.

TARAXACUM OFFICINALE. *Leontodon Taraxacum. Dandelion.*—The herb and root of this plant are used, either singly or together, for the preparation of *Extract of Dandelion*. The herb contains the usual plant-constituents—albumin, gum, sugar, mucilage, &c. The root contains a milky juice, which, on exposure to the air, coagulates, deposits caoutchouc, and acquires a violet-brown colour. John found in it a bitter extractive matter, together with sugar, gum, traces of resin, free vegetable acid, and the ordinary salts. The substance here called gum is doubtless partly inulin (iii. 277), the presence of which in the aqueous extract of dandelion has been demonstrated by Frickinger (Buchn. Repert. xxiii. 45), Widemann (*ibid.* xliii. 281), Overbeck (Arch. Pharm. xxiii. 240), and others. T. and H. Smith (Pharm. J. Trans. viii. 480), by treating the extract of the root prepared with cold water and evaporated to a syrup, with alcohol, obtained a precipitate of albumin, pectin, &c.; and the liquid filtered therefrom deposited, on evaporation, crystals of mannite. They are, however, of opinion that the mannite does not pre-exist in the root, but is produced from cane-sugar, or from inulin, by fermentation, under the influence of the albumin. Perhaps its formation is connected with that of lactic acid, the calcium-salt of which constitutes the deposit often formed in *Mellago taraxaci*, especially after long standing.

The bitter substance of the root, the so-called taraxacin, and the resin, have been examined by Polex (Arch. Pharm. xix. 50). The mliky juice of the root is received in water and heated to the boiling-point, and the liquid is filtered from the coagulum of resin and albumin which forms on cooling. The filtrate, after concentration and further evaporation in free air, at a moderate heat, deposits taraxacin in warty crystals, which may be purified by recrystallisation from water or alcohol. They taste pleasantly bitter, and somewhat sharp; melt easily, giving off inflammable, non-ammoniacal vapours; and dissolve readily in ether, alcohol, and boiling water. Taraxacin also dissolves without alteration in concentrated acids, and is indifferent to most other reagents. (Polex.)

If the coagulum above mentioned be exhausted with boiling alcohol, and the filtrate left to evaporate, resin of taraxacum is deposited, in white cauliflower-like crusts. It melts easily, takes fire with difficulty, is dissolved by ether, not by caustic alkalis, is but slightly attacked by nitric acid, but is dissolved with yellow colour by warm sulphuric acid. The sharp-tasting alcoholic solution is not precipitated by basic acetate of lead (Polex). See also Kromayer (Arch. Pharm. cv. 6), who designates the dried milky juice of dandelion as leontodium.

TARNOWITZITE. Breithaupt's name for the plumbiferous arragonite of Tarnowitz in Upper Silesia, sometimes containing as much as 4 per cent. of plumbic carbonate. It forms prismatic or pointed crystals, and cylindrical aggregates of white or greenish colour. It has a specific gravity of 2·8 to 3·01, and if moistened with sulphuric acid, after ignition, turns first red and then black. According to Websky (Zeitschr. d. deutsch. geolog. Gesellsch. ix. 737), the crystals have the same form as those of arragonite.

TARTAR. A generic name for salts of tartaric acid, but applied especially to the acid tartrate of potassium, which in the crude state, as deposited from fermenting grape-juice, is called crude tartar or argol, and when purified by solution and recrystallisation, cream of tartar.

Crude tartar or argol is of a pale, pinkish, or dark-red colour, according as it is deposited from white or from red wines. It forms a hard crystalline crust, varying in thickness with the character of the grape, the degree of ripeness which it has been allowed to attain, and the peculiarities of the processes adopted in different vineyards. Besides acid tartrate of potassium, which is its essential constituent, it usually contains tartrate of calcium and various impurities. Scheurer-Kestner found in a sample from Tuscany, 73·67 per cent. tartaric acid, 22·13 potash, 0·62 glucose, 0·88 cellulose, 0·32 silica, 0·26 oxide of iron, 1·39 magnesia, and 0·73 colouring-matter. The same chemist gives the following statement of the results of numerous analyses of tartars from various localities :—

Locality.	Quality	Acid Tartrate of Potassium per cent.	Tartrate of Calcium per cent.
Alsace	White	77·50 84·95 85·10	4·6 7·3 9·9
Switzerland	"	73·50 85·90	7·7 18·3
Burgundy	Red	32·10	46·25
Tuscany	White	84·50 85·20 88·50	9·20
Hungary	"	67·30	45·20
Spain	Red	24·20	

The best tartars come from Italy and the South of France.

Tartar is used for the manufacture of tartaric acid, and of carbonate of potassium (iv. 713). For the first mentioned purpose, the presence of a large amount of mucilaginous or other organic matter is very objectionable. To remove this impurity, a considerable proportion of the argol sent to this country is previously submitted to a simple process of purification, which consists in redissolving it in hot water, and adding a small quantity of clay in fine powder. The clay becomes mixed with the flocculent matter, and carries it down to the bottom of the vessel. The clear solution is concentrated and a crop of crystals obtained, which is then called tartar. The repetition of the process yields a proportionally purer article, and tartars are met with in this country, containing from 85 to 98 or 99 per cent. acid tartrate of potassium.

On the other hand, tartars are very often fraudulently adulterated with sulphate and chloride of potassium, sulphate and chloride of calcium, and other cheap materials; so that it is of importance to the manufacturer of tartaric acid to possess a ready method of ascertaining the quantity of tartaric acid contained in them. Now, the direct estimation of tartaric acid is difficult, as none of its salts are insoluble in water; hence it has been usual to estimate the proportion of it in tartars by determining the quantities of potash and lime present, and reckoning both bases as tartrates. Such a method, however, would clearly lead, in the case of adulterated tartars, to an over-estimation of the amount of tartaric acid present. Hence it is necessary to determine not only the amount of bases, but likewise that of the sulphuric, carbonic, or other acids present, besides the tartaric; to calculate the quantities of base required to saturate these acids; and reckon only the remainder as tartrates. An exact and ready method of ascertaining the commercial value of tartars is still a desideratum.

Tartrate of calcium can scarcely be regarded as an impurity in tartar intended for the manufacture of tartaric acid, inasmuch as the first step in the preparation of that acid is to convert the tartrate of potassium into tartrate of calcium. Nevertheless, the presence of a considerable quantity of calcic tartrate in the tartar is objectionable, because it quickly undergoes decomposition under the influence of damp, and is converted into carbonate. For this reason dry storing-places are of great importance for preserving tartars and argols, especially those containing much tartrate of calcium. (See Richardson and Watts's *Chemical Technology*, i. [5], 132, 168.)

TARTAR-EMETIC. Potassio-antimonious tartrate.

TARTARIC ACID. $C^4H^6O^6 = \left.\begin{matrix}(C^4H^2O^2)^{iv}\\ H^4\end{matrix}\right\}O^4$ or $\left.\begin{matrix}H^2\\ (C^4H^2O^2)^{iv}\\ H^2\end{matrix}\right\}O^4$.—This formula represents the composition of five different tetratomic and dibasic acids, some of which agree with one another in nearly all their chemical characters, though they are all distinguished by marked differences of physical properties, especially in their crystalline forms and their relations to polarised light. These five modifications of tartaric acid are:

1. Dextrotartaric or ordinary Tartaric acid, which forms anhydrous, hemihedral, rhombic crystals, and turns the plane of polarisation of a luminous ray to the right.

2. Lævotartaric or Antitartaric acid, which also forms anhydrous, hemihedral, rhombic crystals, but turns the plane of polarisation to the left.

3. Paratartaric or Racemic acid, which forms hydrated, holohedral, triclinic crystals, is optically inactive, and may be separated into dextrotartaric and lævotartaric acids (p. 35).

4. Inactive Tartaric or Mesotartaric acid, which is also without action on polarised light, but is not, like the preceding, resolvable into dextrotartaric and lævotartaric acids.

5. Metatartaric acid, a modification produced by the action of heat upon ordinary tartaric acid, is deliquescent and uncrystallisable; its salts differ from those of ordinary tartaric acid by their crystalline form and greater solubility.

Dextrotartaric and lævotartaric acids resemble one another exactly in specific gravity, solubility, and all their physical properties, excepting crystalline form, action on polarised light, and pyroelectrical relations. Their crystals are bounded by the same number of faces, inclined to one another at exactly the same angles; but they exhibit certain hemihedral faces, which, when the crystals are similarly placed, are situated to the right in the one crystal, and to the left in the other; so that the two crystals, though similar, are not superposible, but are related to one another like an object and its reflected image. Solutions of the two acids of the same strength deflect the plane of polarisation by exactly equal amounts—the one to the right, the other to the left: $[\alpha] = \pm 9{\cdot}6$ (see LIGHT, iii. 675). Both acids exhibit pyroelectricity, but in opposite directions, a crystal of either acid, when heated and left to cool, exhibiting positive electricity on the side on which the hemihedral faces are situated.

The same relations of crystalline form, optical rotatory power, and pyro-electricity, are exhibited by the corresponding metallic salts of dextrotartaric and lævotartaric acids.

When solutions of equal weights of dextro- and lævo-tartaric acids are mixed, the mixture yields by evaporation holohedral crystals of racemic acid. Mixtures of equal weights of the corresponding metallic salts also yield racemates, except in the case of the ammonio-sodic salts (iii. 675).

Dextro- and lævo-tartaric acids further resemble one another exactly in their chemical relations to all substances which have no action on polarised light; but when they come in contact with other optically active substances, this chemical identity no longer exists. In some cases, one of the acids easily forms compounds which cannot be produced with the other; in other cases, the two acids yield compounds identical in composition, but differing considerably in their properties. Thus, dextrotartaric acid combines readily with asparagine, forming a crystalline compound; but lævotartaric acid forms with it only an uncrystallisable syrup. The acid ammonium-salt of dextrotartaric acid forms a crystallisable double salt with the acid ammonium-salt of optically active malic acid; acid lævotartrate of ammonium, on the contrary, does not form a corresponding compound. Dextrotartrate of cinchonine contains 2 at. water of crystallisation, dissolves easily in absolute alcohol, gives off its water and begins to become coloured at 100°; the lævotartrate of cinchonine contains only ½ at. water, but bears a heat of 140° without alteration. The dextro- and lævo-tartrates of quinine, brucine, and strychnine exhibit similar differences (i. 683, 977; v. 24, 442).

The different reactions of the two opposite tartaric acids with optically active substances afford the means of resolving racemic acid into its component acids. When cinchonicine is dissolved in racemic acid, the solution, at a certain degree of concentration, deposits at first crystals of lævotartrate of cinchonicine; from a solution of quinicine in racemic acid, on the other hand, dextrotartrate of quinicine crystallises out first.

Racemic acid may also be decomposed by fermentation. When a few spores of *Penicillium glaucum* are introduced into a solution of racemic acid containing traces of an alkaline phosphate, fermentation is set up, the dextrotartaric acid is decomposed, and if the fermentation be interrupted after a certain time, the liquid contains nothing but lævotartaric acid.

When dextrotartrate of cinchonine is heated for some time to 170°, part of the dextrotartaric acid is converted into lævotartaric acid, and the two combine, forming racemic acid. Lævotartaric acid may be converted into racemic acid in the same manner. Racemic acid is also produced by the action of heat on ethylic tartrate (p. 35). (Pasteur, Ann. Ch. Pharm. lxxii. 164; lxxxiv. 157; lxxxviii. 211; Jahresb. 1847-48, pp. 31, 205; 1849, pp. 127, 307; 1852, p. 175; 1853, p. 423; 1858, p. 248; 1860, p. 250.)

Dextrotartaric Acid, $C^4H^6O^6$. *Ordinary Tartaric Acid. Dextroracemic Acid. Tartersäure. Tartrylsäure. Weinsäure. Weinsteinsäure. Sal essentiale tartari. Acide tartarique.*—This acid was first obtained in the free state by Scheele in 1770, but its existence in tartar had been previously suspected by Duhamel, Marggraf, and Rouelle. It is very widely diffused in the vegetable kingdom, occurring as frequently as citric and malic acid. Its existence in grape-juice, as acid tartrate of potassium, has long been known; the older chemists indeed, Van Helmont and others, were aware that the tartar deposited from wines existed ready-formed in the juice of the grape. It is also found in the free state, or as a potassium- or calcium-salt, in tamarinds, unripe mountain-ash berries, madder-root, potatoes, Jerusalem artichokes, sorrel, girkins, mulberries, pine-apples, black pepper, the leaves of *Chelidonium majus*, the bulbs of *Scilla maritima*, &c.

Dextrotartaric acid is artificially produced:—α. Mostly together with racemic acid, by the oxidation of saccharic acid, and of dextroglucose, cane-sugar, milk-sugar, starch, gum, and sorbin, with nitric acid (p. 35).—β. By boiling acid bromomalate of calcium (iii. 795) with lime-water. Acids having the composition of tartaric are also said to be produced.—γ. From citric acid, when lemon-juice is kept for a year in bottles (Schindler, Ann. Ch. Pharm. xxxi. 280).—δ. From a solution of pyroxylin in potash (Kerckhoff and Reuter, J. pr. Chem. xlvi. 284); but it is not stated whether these acids are identical in physical properties with dextrotartaric acid. The acid $C^4H^6O^6$, obtained by boiling the silver-salt of dibromosuccinic acid with water, or its calcium-salt with lime-water, is optically inactive. (Kekulé, p. 459.)

Preparation.—Tartaric acid is always prepared from acid tartrate of potassium—on the small scale from the purified salt (cream of tartar), on the large scale from partially purified tartars or crude argols. A boiling solution of the acid tartrate is first treated with pounded chalk or whiting, to convert it into insoluble sulphate of calcium and soluble neutral tartrate of potassium:

$$2C^4H^5KO^6 + Ca''CO^3 = C^4H^4K^2O^6 + C^4H^4Ca''O^6 + H^2O + CO^2.$$

The mixture is thrown on a filter; and the filtered solution of neutral potassic tartrate is mixed with solution of calcic chloride, or with precipitated calcic sulphate, obtained from a previous operation, whereby the whole of the tartaric acid is precipitated as tartrate of calcium. The two lime-precipitates are then boiled with a quantity of dilute sulphuric acid sufficient to convert the whole of the calcium into sulphate; and the filtered solution of tartaric acid is evaporated to a syrup at a gentle heat, then left to itself in a warm place, where it deposits an additional quantity of calcic sulphate, and finally transferred to the crystallising vessels. The presence of an excess of sulphuric acid greatly favours the crystallisation of the tartaric acid, but it acts injuriously during the subsequent evaporation of the mother-liquors, as it becomes more and more concentrated, and ultimately decomposes a considerable quantity of the tartaric acid still remaining in solution. (For details of the manufacturing process, see Richardson and Watts's *Chemical Technology*, vol. i. pt. v. p. 138.)

Lævotartaric Acid, $C^4H^6O^6$. *Antitartaric Acid. Lævoracemic Acid.*—The formation of this acid by the decomposition of racemic acid has already been mentioned. When equal weights of racemic acid are saturated, the one with soda, the other with ammonia, and mixed, the mixture deposits, on cooling or spontaneous evaporation, large beautiful crystals of a double salt, all of which are hemihedral, one half of them having the hemihedral forces oppositely situated to those of the other half; and on carefully separating these two kinds of crystals (the solutions of which exhibit equal and opposite actions on polarised light), purifying them by recrystallisation, precipitating the solutions by nitrate of lead, and decomposing the lead-salts with sulphuric or sulphydric acid, solutions are obtained which on evaporation yield crystals—the one of dextrotartaric acid, agreeing exactly in character with those obtained from tartar, as above described; the other of lævotartaric acid, agreeing with dextrotartaric acid in all respects, excepting in the opposite hemihedry of its crystals, and the opposition of its optical and pyro-electric properties. Respecting the preparation of lævotartaric acid by the fermentation of racemic acid, and by the action of heat on the racemates of cinchonicine and quinicine, see p. 673.

Properties.—Tartaric acid crystallises in monoclinic prisms, having the axes $a : b : c = 0{\cdot}7845 : 1 : 0{\cdot}8054$. Angle $b : c = 79° 43'$; $\infty P : \infty P$ (orthod.) $= 102° 52'$; $[P\infty] : [P\infty]$ (clinod.) $= 89° 26'$; $-P\infty : c = 45° 0'$; $+P\infty : c = 57° 30'$. Ordinary combination $\infty P . \infty P\infty . -P\infty . +P\infty$ (the last often wanting) . $[P\infty]$. The faces $[P\infty]$ are often developed only at one extremity of the orthodiagonal, and on one or the other side of the crystals, according as the acid is dextro- or lævo-rotatory. These faces are often greatly predominant.

The crystals are colourless and transparent, and do not contain any water of crystallisation; their specific gravity is 1·75 (Richter); 1·739 (Buignet, Jahresb. 1861, p. 15). They are very soluble in water and in alcohol, insoluble in ether; the aqueous solution becomes covered, after a while, with a fungous growth. The quantities of the crystallised acid contained in aqueous solutions of different densities are as follows (Schiff, Jahresb. 1859, p. 41):

Weight of crystallised acid in 100 pts. of solution.	Specific gravity of solution at 15°.
33	1·1654
22	1·1062
14·66	1·0690
11	1·0511
7·33	1·0337
3·67	1·0167

On mixing the concentrated solutions of dextro-, and lævo-tartaric acid, crystals of racemic acid are abundantly deposited, with evolution of heat quite perceptible to the hand.

Respecting the molecular rotatory power and the pyro-electricity of the two opposite tartaric acids, see p. 672. Their pyro-electricity is very strong, the heat of the hand developing it sufficiently to affect a sensitive electroscope.

The solution of tartaric acid forms white precipitates with the aqueous solutions of caustic *baryta, strontia, lime,* and *acetate of lead,* but it does not precipitate the chloride of barium, strontium, or calcium. Tartaric acid is distinguished from racemic acid by the greater solubility of its calcium-salt (p. 36).

Tartaric acid added in excess to the solution of a *potassium-salt* forms a white crystalline precipitate of acid potassic tartrate, provided the solution is not too dilute: the addition of alcohol renders the reaction much more delicate: the formation of the precipitate rated by stirring, and by rubbing the sides of the vessel with a glass rod. The precipitate is soluble in free alkalis, which convert it into neutral tartrate; hence, for detecting small quantities of tartaric acid in a solution, free potash should not be used, but rather chloride or nitrate of potassium, an excess of which does not dissolve the acid tartrate. Tartaric acid may be detected in presence of a considerable quantity of citric acid by mixing the solution with acetate of potassium, and an equal volume of strong alcohol. On the other hand, a small quantity of citric acid may be detected in the midst of a large quantity of tartaric acid, by removing the latter as above, evaporating the alcoholic filtrate, and treating the residue with chloride of calcium at the boiling heat (i. 995). (Spiller, Chem. Soc. Qu. J. x. 110; see also Schnitzer, Jahresb. 1862, p. 626.)

Decompositions.—1. Tartaric acid melts between 170° and 180°, and is gradually converted, without loss of water, into the isomeric compound, metatartaric acid (p. 688). By prolonged heating, water is eliminated, and tartralic or ditartaric acid, $C^8H^{10}O^{11} = 2C^4H^6O^6 - H^2O$, is produced; then tartrelic acid, $C^4H^4O^5 = C^4H^6O^6 - H^2O$; and ultimately insoluble tartaric anhydride, isomeric with the last. If the heat be increased, decomposition takes place, resulting in the formation of pyrotartaric and pyroracemic acids (iv. 769-771), together with acetic acid, formic acid, aldehyde, furfurol, ethylene, carbonic anhydride, &c.

2. Tartaric acid heated with fused *hydrate of potassium* is resolved into acetic and oxalic acids:

$$C^4H^6O^6 = C^2H^4O^2 + C^2H^2O^4.$$

3. By the *oxidation* of tartaric acid (*e.g.* by the action of chromates, permanganates, peroxide of manganese, peroxide of lead, minium, &c.), carbonic anhydride and formic acid are generally produced. The solution of the acid warmed with salts of *silver*, *gold*, and *platinum*, reduces the metals. By slow oxidation, especially by the spontaneous decomposition of nitrotartaric acid, an oxidation-product less removed from tartaric acid is formed—namely, tartronic acid:

$$\underset{\substack{\text{Tartaric}\\\text{acid.}}}{C^4H^6O^6} + O^3 = \underset{\substack{\text{Tartronic}\\\text{acid.}}}{C^3H^4O^5} + H^2O + CO^2.$$

4. By the action of *hydriodic acid* or *iodide of phosphorus*, tartaric acid is reduced to malic or to succinic acid:

$$\underset{\substack{\text{Tartaric}\\\text{acid.}}}{C^4H^6O^6} + 2HI = H^2O + I^2 + \underset{\substack{\text{Malic}\\\text{acid.}}}{C^4H^6O^5}.$$

$$\underset{\substack{\text{Tartaric}\\\text{acid.}}}{C^4H^6O^6} + 4HI = 2H^2O + 2I^2 + \underset{\substack{\text{Succinic}\\\text{acid.}}}{C^4H^6O^4}.$$

5. With *pentachloride of phosphorus*, tartaric acid yields chloromaleic chloride, $C^4HClO^2.Cl^2$. (Perkin and Duppa; see Maleic Acid, iii. 788.)

6. Pulverised tartaric acid, digested for several hours with *chloride of acetyl*, is converted into diacetotartaric anhydride, $C^8H^8O^7$ (Perkin, Chem. Soc. Qu. J. xx. 150):

$$C^4H^6O^6 + 2C^2H^3OCl = 2HCl + H^2O + C^4H^2(C^2H^3O)^2O^5.$$

7. Tartaric acid heated to 150° in a sealed tube, with an equivalent quantity of *benzoic acid*, yields benzotartaric acid, $C^{11}H^{10}O^7 = C^4H^5(C^7H^5O)O^6 = C^4H^6O^6 + C^7H^6O^2 - H^2O$. (Dessaignes, J. Pharm. [3] xxxii. 47.)

8. Tartaric acid is decomposed by strong *sulphuric acid* and by *nitric acid*. With very strong nitric acid it forms nitrotartaric acid.—*Chlorine* and *bromine* act but slightly upon the aqueous solution.

9. The *fermentation* of crude tartrate of calcium yields butyracetic acid. (Nöllner, i. 688.)

10. Tartaric acid heated with *alcohols*, monatomic or polyatomic, forms ethers, with elimination of water; in like manner with cane-sugar, glucose, dulcite, quercite, and other saccharoïdal substances. (See Tartaric Ethers.)

Tartrates.—Tartaric acid, as already observed, is tetratomic, and for the most part dibasic, 2 of the hydrogen-atoms in the molecule, $\left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\H^2\end{matrix}\right\}O^4$, being easily replaceable by metals, and the other two by alcoholic or acid radicles. With monatomic metals, it forms acid, neutral, and double salts, like the following:

$$\underset{\substack{\text{Acid potassic}\\\text{tartrate.}}}{\left.\begin{matrix}H^2\\C^4H^2O^2\\H.K\end{matrix}\right\}O^4} \qquad \underset{\substack{\text{Neutral potassic}\\\text{tartrate.}}}{\left.\begin{matrix}H^2\\C^4H^2O^2\\K^2\end{matrix}\right\}O^4} \qquad \underset{\substack{\text{Sodio-potassic}\\\text{tartrate.}}}{\left.\begin{matrix}H^2\\C^4H^2O^2\\Na.K\end{matrix}\right\}O^4}$$

With diatomic metals, it forms neutral salts, $C^4H^4M''O^6$, and double salts consisting of a double molecule of the acid, in which 2 at. hydrogen are replaced by a diatomic metal and 2 at. more by an alkali-metal; *e.g.*:

$$\left.\begin{matrix}H^2\\C^4H^2O^2\\Ba''\end{matrix}\right\}O^4 \qquad\qquad \left.\begin{matrix}H^4\\(C^4H^2O^2)^2\\Ba''K^2\end{matrix}\right\}O^8$$

Neutral baric tartrate. **Baric potassic tartrate.**

With triatomic metals, tartaric acid forms a peculiar class of salts—best known in the case of antimony—the constitution of which may be illustrated by the following formulæ:

$$\left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\H.Sb'''\end{matrix}\right\}\begin{matrix}O^4\\O\end{matrix} \qquad \left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\K.Sb'''\end{matrix}\right\}\begin{matrix}O^4\\O\end{matrix} \qquad \left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\\overset{'''}{Sb}{}^2\end{matrix}\right\}\begin{matrix}O^4\\O^2\end{matrix}$$

Acid antimonious tartrate. **Potassio-antimonious tartrate.** **Neutral antimonious tartrate.**

These formulæ are a typical expression of the idea that one of the three atomicities of the antimony takes the place of 1 at. of the typical hydrogen of the tartaric acid, binding instead of it one atomicity of the typical oxygen (Kekulé). The same salts may, however, be formulated similarly to the ordinary tartrates, by supposing 1 at. of the basic hydrogen to be replaced by the monatomic radicle antimonyl SbO; thus:

$$\left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\H.SbO\end{matrix}\right\}O^4 \qquad \left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\K.SbO\end{matrix}\right\}O^4 \qquad \left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\(SbO)^2\end{matrix}\right\}O^4$$

Acid antimonious tartrate. **Potassio-antimonious tartrate.** **Neutral antimonious tartrate.**

When these salts are heated to 160°—200°, they give off water, and form compounds which may be regarded either as tartrates in which the triatomic antimony replaces three-fourths of the typic hydrogen of the acid:

$$\left.\begin{matrix}(C^4H^2O^2)^{iv}\\H.Sb'''\end{matrix}\right\}O^4 \qquad\qquad \left.\begin{matrix}(C^4H^2O^2)^{iv}\\K.Sb'''\end{matrix}\right\}O^4;$$

or as antimonylic derivatives of the first anhydride of tartaric acid:

$$\left.\begin{matrix}(C^4H^2O^2)^{iv}\\H.SbO\end{matrix}\right\}O^3 \qquad \left.\begin{matrix}(C^4H^2O^2)^{iv}\\K.SbO\end{matrix}\right\}O^3 \qquad \left.\begin{matrix}(C^4H^2O^2)^{iv}\\(SbO)^2\end{matrix}\right\}O^2.$$

Tartaric acid forms similar compounds with arsenic and with boron. (Kekulé's *Lehrbuch*, ii. 201.)

The first of the formulæ above given for the antimony-salts dried at 160°—200° represents tartaric acid as tetrabasic; and this view is further in accordance with the known existence of a tetraplumbic tartrate (p. 682); but in most of its relations, tartaric acid, as already observed, is only dibasic.

The neutral tartrates of the *alkali-metals* are very soluble in water; the acid tartrates of potassium and ammonium are sparingly soluble; all tartrates are insoluble in alcohol. Hence, tartaric acid dissolved in alcohol does not decompose carbonates. The neutral tartrates of the *earth-metals* and *heavy metals* are, for the most part, insoluble or sparingly soluble in water, but dissolve in aqueous tartaric acid, also in hydrochloric and in nitric acid; also, with exception of the silver- and mercury-salts, in excess of potash or soda. Ammonia likewise dissolves all tartrates, excepting tartrate of mercury.

Tartaric acid added to the solutions of most metallic salts prevents their precipitation by alkalis. According to Aubel and Ramdohr (Ann. Ch. Pharm. ciii. 33; Jahresb. x. 572), metallic oxides may be divided, according to their behaviour with caustic potash or soda in presence of tartaric acid, into the three following groups:—*α*. Oxides soluble in the alkali in presence of tartaric acid, and not precipitated on boiling: alumina, bismuth-oxide, chromic oxide, cobaltous oxide, cupric oxide, ferric oxide, glucina, lead-oxide, nickel-oxide, platinic oxide, zinc-oxide.—*β*. Oxides precipitated on boiling from the alkaline solution, if moderately dilute: auric oxide (reduced on boiling), cadmium-oxide, manganous oxide, uranic oxide.—*γ*. Insoluble: mercuric oxide, silver-oxide (reduced on boiling), stannous oxide. (See further H. Grothe, J. pr. Chem. xcii. 175; Jahresb. 1864, p. 686.)

Most of the soluble tartrates crystallise easily, and some (especially the double salts) form large well-defined crystals. The crystals are invariably hemihedral, and their solutions turn the plane of a polarised ray to the right or to the left, according to the position of the hemihedral faces. The dextro- and lævo-tartrates are likewise opposite in their pyro-electric properties. In all their other characters they resemble one another exactly, and the solution of a dextrotartrate mixed with that of an equal weight of the corresponding lævotartrate forms a mixture which yields holohedral and optically inactive crystals of the corresponding racemate, excepting in the case of the sodio-ammonic salts, which crystallise out separately, as dextro- and lævo-tartrates (p. 674).

Tartrates calcined in contact with the air give off the odour of burnt sugar. Their dilute aqueous solutions become covered after a while with fungi.

The composition of the tartrates has been established chiefly by the analyses of Berzelius (Pogg. Ann. xix. 305, xxxvi. 4; Ann. Ch. Phys. [2], lxvii. 303), Dulk (Schw. J. lxiv. 180, 193), Werther (J. pr. Chem. xxxii. 383), and Dumas and Piria (Ann. Ch. Phys. [3] v. 353): see also *Gmelin's Handbook*, x. 273–326. The crystalline forms of a great number of tartrates have been determined by De la Provostaye (Ann. Ch. Phys. [3], iii. 129) and Pasteur, and their optical properties by Biot and Pasteur (see references, p. 673).

a. *Tartrates containing only Monatomic Metals.*

TARTRATES OF AMMONIUM.—The *neutral salt*, $C^4H^4(NH^4)^2O^6$, is obtained by evaporating a solution of the acid, neutralised with ammonia or carbonate of ammonium, in prismatic crystals, which are very soluble in water, and effloresce, with loss of ammonia, on exposure to the air. The crystals are monoclinic, having the axes $a : b : c = 0·868 : 1 : 1·244$. Angle $b : c = 88° 9'$; $[P\infty : P\infty]$ (clinod.) $= 69° 50'$; $+ P\infty : c = 39° 31'$. Ordinary combination, $oP . \infty P\infty . + P\infty . [P\infty]$; also with $+ P$ and $- P$ subordinate. Cleavage perfect parallel to oP. The faces $[P\infty]$ are present in only half the number required by the law of symmetry: the crystals are therefore hemihedral. Rotatory power $[\alpha]_r = \pm 29°$. Specific gravity of the crystals = 1·566. (Schiff, Jahresb. 1859, p. 16.)

The *acid salt*, or *bitartrate of ammonia*, $C^4H^5(NH^4)O^6$, is precipitated, on adding tartaric acid to the solution of the neutral salt, as a crystalline powder, exhibiting under the microscope beautiful shining laminæ, forming oblique-angled parallelograms or hexagonal plates, elongated and often hemitropic. It is slightly soluble in cold, very soluble in boiling water. The crystals are trimetric, and isomorphous with the acid potassium-salt. Axes $a : b : c = 0·6933 : 1 : 0·7086$. Angle $P : P$ (brach.) $= 127° 18'$; $P : P$ (macr.) $= 100° 20'$; $P : P$ (basal) $= 102° 24'$; $\infty P : \infty P$ (macr.) $= 69° 28'$; $\bar{P}\infty : \bar{P}\infty$ (basal) $= 70° 38'$; $2\breve{P}\infty : 2\breve{P}\infty$ (basal) $= 109° 36'$; $3\breve{P}\infty : 3\breve{P}\infty = 129° 36'$. The crystals exhibit the same faces as those of the acid potassium-salt (p. 678), and cleave most easily parallel to oP. They are hemihedral, the P-faces being always unequally developed; four of them, two at each end, being very small or non-existent, whilst the other four, which are much larger, are so situated as to form, by sufficient prolongation, the irregular tetrahedron $\frac{P}{2}$ (De la Provostaye). According to Hahn (Jahresb. 1859, p. 286), the crystals exhibit the combination $\infty P . \infty\breve{P}\frac{3}{2} . \infty\bar{P}2 . \infty\bar{P}\infty . P . \bar{P}\infty$; axes $a : b : c = 0·72988 : 1 : 0·83425$; angle $\infty P : \infty\breve{P}$ (macr.) $= 72° 15'$; $\bar{P}\infty : \bar{P}\infty$ (over c) $= 100° 20'$. The specific gravity of the crystals is 1·680. (Schiff.)

Acid dextrotartrate of ammonium combines with optically active acid malate of ammonium, forming the salt $C^4H^5(NH^4)O^6.C^4H^5(NH^4)O^5$, which crystallises in thick acuminated prisms (Pasteur). The acid lævotartrate does not form a similar compound.

TARTRATES OF CÆSIUM.—The *neutral tartrate* is very deliquescent (Bunsen).—The *acid salt*, $C^4H^5CsO^6$, crystallises in rhombic prisms, isomorphous with the rubidium-salt. Axes $a : b : c = 0·694 : 1 : 0·661$. Angle $P : P$ (brach.) $= 128° 50'$; $P : P$ (macr.) $= 103°$; $P : P$ (basal) $= 98° 30'$. Observed combination, $\infty\bar{P}\infty . \infty\breve{P}\infty . \infty P$ (the latter very subordinate and imperfect), together with the sphenoïds $+\frac{P}{2}$, $-\frac{P}{2}$, and $-\frac{\frac{4}{3}P3}{2}$. The crystals are dextro- or lævo-rotatory, according as one or the other of the sphenoïdal faces $\frac{P}{2}$ is absent or subordinate (they rarely occur together); the faces $-\frac{\frac{4}{3}P3}{2}$ occur only in lævo-rotatory crystals. Cleavage perfect parallel to $\infty\bar{P}\infty$ and $\infty\breve{P}\infty$, both of which faces are striated parallel to the principal axis. The striation and cleavage distinguish the crystals from those of acid potassic tartrate, to which they bear a general resemblance (J. P. Cooke, Sill. Am. J. [2], xxxvii. 70). They disolve in 10·3 pts. water at 25°, and in 1·02 pt. boiling water. (Allen, *ibid.* xxxiv. 367.)

TARTRATES OF LITHIUM.—The *neutral salt* is white, deliquescent, and uncrystallisable.—The *acid salt*, $2C^4H^5LiO^6.3H^2O$, forms small crystals, very soluble in water. (Dulk.)

TARTRATE, MERCUROUS.—This salt is obtained, by precipitation, as a white crystalline powder, or in the form of shining needles or scales. It is insoluble in water, but very soluble in nitric acid. Boiling water decomposes and turns it grey.

TARTRATES OF POTASSIUM.—The *neutral salt*, $C^4H^4K^2O^6$, prepared by saturating the acid salt with carbonate of potassium, crystallises with difficulty in short monoclinic prisms, the faces of which have generally very little lustre. Axes $a : b : c = 0·4021 : 1 : 1·1085$. Angle $b : c = 75° 1 2'$; $\infty P : \infty P$ (orthod.) $= 134° 50'$; $+P\infty : c = 52° 5'$; $-P\infty : c = 37° 25'$. The most frequently occurring faces are: ∞P, oP, $\infty P\infty$, $[\infty P\infty]$, $+P\infty$, $-P\infty$; more rarely $+\frac{1}{2}P$ occurs. Cleavage parallel to $+P\infty$ and $-P\infty$.

One part of neutral potassic tartrate dissolves in 0·75 pt. water at 2°, in 0·66 pt. at 14°, in 0·63 pt. at 23°, and in 0·47 pt. at 64° (Osann). It is very slightly soluble in boiling alcohol. Most acids added to the solution of this salt precipitate the acid tartrate; bromine forms the same precipitate without attacking the tartaric acid.

The *acid salt, bitartrate of potash*, or *cream of tartar*, $C^4H^5KO^6$, is contained in grape-juice, and, being much less soluble in alcoholic liquids than in water, is deposited, during the vinous fermentation of the juice, in crystalline crusts, called crude tartar or argol. The same deposit is formed in many kinds of wine when kept in casks or bottles, and constitutes the well-known crust of port-wine. The salt likewise exists in many other vegetable juices. Crude tartar, when purified by recrystallisation, yields cream of tartar. The pure salt is also formed whenever tartaric acid is added in excess to the solution of a potassium-salt.

The crystals of acid potassic tartrate belong to the trimetric system, and are isomorphous with the acid ammonium-salt. Axes $a : b : c = 0·7115 : 1 : 0·7372$. Angle $P : P$ (brach.) $= 125° 46'$; $P : P$ (macr.) $= 100° 20'$; $P : P$ (basal) $= 103° 28'$; $\infty P : \infty P$ (macr.) $= 70° 52'$; $\breve{P}\infty : \breve{P}\infty$ (basal) $= 72° 48'$; $2\breve{P}\infty : 2\breve{P}\infty = 111° 42'$; $3\breve{P}\infty : 3\breve{P}\infty = 131° 20'$. Ordinary combination $P . \infty P$, with $\infty\breve{P}\infty$ and the above-mentioned brachydiagonal domes. One half of the crystals is generally sphenoïdically enlarged in comparison with the other half. Cleavage most distinct parallel to oP. Specific gravity of the crystals = 1·973 (Schiff); 1·956 (Buignot).

Acid tartrate of potassium is but slightly soluble in water, requiring for solution about 240 pts. of water at 10°, and 15 pts. of boiling water. It is insoluble in strong alcohol, but dissolves easily in concentrated mineral acids and in alkalis, which convert it into the neutral tartrate.

The following determinations of the solubility of acid potassic tartrate in water, at various temperatures, have been made by Alluard (Compt. rend. lix. 500; Jahresb. 1864, p. 94) and by Chancel (Compt. rend. lx. 408; Jahresb. 1865, p. 830), in pure water and in water containing 10·5 per cent. alcohol. Alluard's determinations were made under a barometrical pressure of 718 mm.:—

Solubility of Cream of Tartar, $C^4H^5KO^6$.

Temperature.	Quantities of Salt dissolved in 100 pts. by weight of water.		Quantities of Salt dissolved in 100 pts. by weight of water containing 10·5 per cent. alcohol.
	Alluard.	Chancel.	Chancel.
0°C.	0·32	0·24	0·14
5		0·30	0·175
10	0·40	0·37	0·21
15		0·45	0·25
20	0·57	0·55	0·305
25		0·67	0·37
30	0·90	0·805	0·46
35		0·96	0·57
40	1·31	1·13	0·70
50	1·81		
60	2·40		
70	3·20		
80	4·50		
90	5·70		
100	6·90		

A saturated aqueous solution boils at 99·6° (Alluard). The solubility of the salt in water or in dilute alcohol is not diminished by the presence of glucose. ([illegible]el.)

The aqueous solution reddens litmus-paper, and dissolves a considerable number of metallic oxides, forming double tartrates.

Cream of tartar, when calcined, emits a pungent odour like that of burnt bread, and leaves a residue of potassic carbonate, mixed with charcoal, the *Sal fixum tartari* of the older chemists; calcined with saltpetre, it yields, according to the proportions, the *black* or *white flux* used in metallurgical and assaying operations.

Cream of tartar is one of the mordants most frequently employed in the dyeing of wool. Mixed with pounded chalk and alum, it forms an excellent powder for cleaning silver.

Ammonio-potassic tartrate, $C^4H^4(NH^4)KO^6$, obtained by saturating cream of tartar with ammonia or its carbonate, forms monoclinic crystals isomorphous with neutral potassic tartrate. They alter quickly in the air, giving off ammonia, and are very soluble in water.

Lithio-potassic tartrate, $C^4H^4LiKO^6.H^2O$, is very soluble in water, and, according to Zepharovich (Wien. Akad. Ber. xli. 520), crystallises in large rhombic prisms, having the axes $a : b : c = 0{\cdot}5477 : 1 : 0{\cdot}4430$; angle $\infty P : \infty P$ (brach.) = 122° 34′; $P : \infty P$ = 132° 41′. They exhibit the combination $\infty P \,.\, \infty\breve{P}\frac{3}{2} \,.\, \infty\breve{P}2 \,.\, \infty\breve{P}\infty \,.\, P \,.\, oP$, hemihedral from predominance or exclusive development of four of the P-faces. Cleavage imperfect parallel to oP.

TARTRATES OF RUBIDIUM.—The *neutral salt* has not been described.—The *acid salt*, $C^4H^5RbO^6$, is isomorphous with the acid cæsium-salt, exhibiting the same faces with the exception of $-\frac{4P3}{2}$, also the same striation and cleavage. Axes $a : b : c = 0{\cdot}726 : 1 : 0{\cdot}695$. Angle $P : P$ (brach.) = 126° 43′; $P : P$ (macr.) = 103° 40′; $P : P$ (basal) = 99° 34′ (J. P. Cooke). The crystals are permanent in the air, at ordinary temperatures, and at 100° they dissolve in 8·45 pts. water at 25°, and in 8·5 pts. of boiling water. The great difference of solubility between this and the cæsium-salt affords a means of separating the two metals by fractional crystallisation of their acid tartrates. (Allen.)

TARTRATE OF SILVER, $C^4H^4Ag^2O^6$.—This salt is obtained, as an amorphous curdy precipitate, on mixing a cold dilute solution of silver-nitrate with a dilute solution of Rochelle-salt slightly acidulated with nitric acid: if the solutions are mixed at the boiling heat, the mixture turns brown, and deposits brown laminæ of metallic silver. If a hot moderately strong solution of Rochelle-salt be added to a dilute solution of silver-nitrate, and the liquid heated to 80°, till the precipitate begins to be permanent (a certain quantity of the silver-nitrate remaining undecomposed), the filtered solution, on cooling, yields tartrate of silver, in white scales having a metallic lustre.

Tartrate of silver is nearly insoluble in water. It blackens on exposure to light, and, when heated, gives off carbonic anhydride and pyrotartaric acid, leaving a spongy shining residue of metallic silver. The dry salt is quickly decomposed by chlorine, yielding chloride of silver and empyreumatic products. When chlorine is passed into water in which tartrate of silver is suspended, carbonic anhydride is given off, and chloride of silver is obtained, together with unaltered tartaric acid.

A solution of tartrate of silver in ammonia deposits metallic silver at the boiling heat, while the liquid retains in solution a peculiar ammoniacal salt, which is less soluble in water than tartrate of ammonium, and crystallises on cooling.—Caustic *potash* and *soda* decompose tartrate of silver at ordinary temperatures, oxide of silver being separated, and the liquid apparently retaining potassio-argentic or sodio-argentic tartrate. (Liebig and Redtenbacher, Ann. Ch. Pharm. xxxviii. 132.—Erdmann, J. pr. Chem. xxv. 504.)

TARTRATES OF SODIUM.—The *neutral salt*, $C^4H^4Na^2O^6.2H^2O$, crystallises in trimetric prisms having the axes $a : b : c = 0{\cdot}7696 : 1 : 0{\cdot}3366$. Angle $\infty P : \infty P$ (brach.) = 104° 50′; $\infty P : \breve{P}\infty$ = 108° 31′; $\breve{P}\infty : \breve{P}\infty$ (basal) = 132° 44′; $\infty P : \infty\bar{P}\infty$ = 142° 25′; $\infty P : \infty\breve{P}\infty$ = 127° 35′. Ordinary combination $\infty P \,.\, \infty\breve{P}\infty \,.\, \infty\bar{P}\infty \,.\, \breve{P}\infty$ (De la Provostaye). The crystals have a specific gravity of 1·794 (Buignet). They are limpid, permanent in the air, soluble in 5 pts. of cold water, very soluble in hot water, insoluble in absolute alcohol. When heated, they melt in their water of crystallisation. By rapid crystallisation the salt is obtained in tufts of needles.

The *acid salt*, $C^4H^5NaO^6.H^2O$, is formed on mixing a hot solution of the neutral salt with ½ pt. tartaric acid, and separates in crystals on cooling. It dissolves in 9 pts. of cold and 1·8 pt. boiling water, but is insoluble in alcohol. It is difficult to obtain this salt in large crystals, but, by leaving a drop of the hot solution to evaporate under the microscope, small beautifully defined crystals soon make their appearance, having the form of right rhombic prisms ∞P, bevelled at each end by the hemihedral faces $\frac{P}{2}$.

Ammonio-sodic tartrate, $C^4H^4Na(NH^4)O^6.4H^2O$, is obtained by saturating acid tartrate of ammonium with carbonate of sodium, and concentrating the solution; also by mixing the warm solutions of equivalent quantities of the sodium- and ammonium-salts of racemic acid, and cooling the solution, or leaving it to evaporate, dextro- and lævo-tartrate of sodium and ammonium being then deposited in equal quantities. The crystals, which are often of considerable size, are trimetric, and isomorphous with those of the potassio-sodic salt. Axes $a : b : c = 0{\cdot}8233 : 1 : 0{\cdot}4200$. Angle $\infty P : \infty P$ (macr.) = 78° 36′; $\infty\bar{P}2 : \infty\bar{P}2$ (macr.) = 44° 44′; $\bar{P}\infty : \bar{P}\infty$ (basal) = 54° 4′; $\breve{P}\infty : \breve{P}\infty$ (basal) = 45° 34′; $2\breve{P}\infty : 2\breve{P}\infty$ (basal) = 80° 4′. Ordinary combination $\infty P \,.\, \infty\bar{P}2$ (often predominant) $.\ \infty\bar{P}\infty \,.\, \infty\breve{P}\infty \,.\, \bar{P}\infty \,.\, 2\breve{P}\infty \,.\, \breve{P}\infty \,.\, oP \,.\, \pm\frac{P}{2}$, the hemihedral faces being situated on one side or the other of the crystals, according as the salt is dextro- or lævo-rotatory. Rotatory power $[\alpha]_j = \pm 26°$. Specific gravity of the crystals = 1·587. (Schiff.)

Lithio-sodic tartrate, $C^4H^4LiNaO^6.2H^2O$, resembles the lithio-potassic salt.

Potassio-sodic tartrate, *Rochelle* or *Seignette salt*, $C^4H^4KNaO^6.4H^2O$.—This splendid salt is prepared by adding, in small portions and successively, 4 pts. cream of tartar, and about 3 pts. of crystallised sodic carbonate, to 12 pts. of boiling water. When the whole has been added, the liquid must be tested, to ensure that it is slightly alkaline, and then concentrated by evaporation. On cooling, it deposits fine large crystals of the double salt, and the mother-liquors yield an additional quantity; after a certain time, however, they deposit nothing but needles of sodic tartrate; but by redissolving these, and adding cream of tartar, an additional quantity of Rochelle-salt may be obtained. The crystals, which are often very large, are rhombic prisms, isomorphous with the preceding salt. Axes $a : b : c = 0{\cdot}8317 : 1 : 0{\cdot}4296$. Angle $\infty P : \infty P$ (macr.) = 79° 30′; $\infty\bar{P}2 : \infty\bar{P}2$ (macr.) = 45° 10′; $\bar{P}\infty : \bar{P}\infty$ (basal) = 54° 38′; $\breve{P}\infty : \breve{P}\infty$ (basal) = 46° 30′; $2\breve{P}\infty : 2\breve{P}\infty$ (basal) = 81° 20′. The crystals exhibit, for the most part, the same faces as the ammonio-sodic salt; $\breve{P}\infty$, however, is usually but slightly developed. Specific gravity = 1·767 (Schiff); 1·790 (Buignet).

The crystals melt in their water of crystallisation between 70° and 80°, forming a transparent liquid, which begins to boil at 120°, the ebullition continuing till the temperature rises to 215°, by which time all the water (amounting to 25·1 per cent.) is driven off. The residue is a viscid mass, which remains transparent when cold, and absorbs moisture from the air (Fresenius, Ann. Ch. Pharm. liii. 234).—The dry salt dissolves in 2·62 pts. water at 6° (Fresenius). The crystals dissolve in 3·3 pts. water at 3°, in 2·4 pts. at 11°, and in 1·5 pt. at 26° (Osann); in 2 pts. at 5·6°, in 1·2 pts. at 12·5°, in 0·42 pt. at 25°, and in 0·3 pt. at 37·5° (Brandes). The solution saturated at 8° has a density of 1·254.

Rubidio-sodic tartrate, $C^4H^4RbNaO^6.4H^2O$.—The solution of this salt, when left to evaporate spontaneously, solidifies to a transparent jelly; but, by slow cooling of a hot solution, crystals are obtained isomorphous with Rochelle-salt, and exhibiting the same faces, with addition of $2\bar{P}2$ and $2\bar{P}\infty$. (Piccard, Jahresb. 1864, p. 125.)

TARTRATES OF THALLIUM.—The *neutral salt*, $C^4H^4Tl^2O^6$, is slightly soluble in water and in alcohol. The crystals, which usually occur as twins, appear to be trimetric, but different in form from the neutral ammonium- and potassium-salts. De la Provostaye gives, as approximate measurements of the angles, $\infty P : \infty P$ (macr.) = 60°; $\infty P : \infty\breve{P}$, = 120°; . $\infty\breve{P}\infty : \breve{P}\infty$ = 131°; $\infty P : \breve{P}\infty$ = 110°. The crystals are anhydrous alterable in the air, become carbonised at 170°, and at higher temperatures leave yellow oxide of thallium, with a small quantity of reduced metal.

The *acid salt*, $C^4H^5TlO^6$, is precipitated, on adding tartaric acid to a solution of the neutral salt, in small flat prisms, which are difficult to measure. De la Provostaye gives, as approximate angular values, $\infty\bar{P}\infty : \infty P$ = 123°; $\breve{P}\infty : \breve{P}\infty$ = 108° to 110°; $\infty\breve{P}\infty : \breve{P}\infty$ = 125° to 126°; these angles are nearly the same as in the acid tartrates of ammonium and potassium. This salt is less soluble than the neutral tartrate of thallium. (Kuhlmann, Jahresb. 1862, p. 188.)

β. *Tartrates containing Diatomic Metals.*

TARTRATE OF BARIUM, $C^4H^4Ba''O^6$, is precipitated, on mixing tartrate of potassium with chloride of barium, or tartaric acid with baryta-water, in white flocks, which become crystalline when left at rest; it is insoluble in excess of tartaric acid.

Potassio-baric tartrate, $C^8H^8Ba''K^2O^{12}.2H^2O$, or $C^4H^4Ba''O^6.C^4H^4K^2O^{12}.2H^2O$, is obtained, as a sparingly soluble pulverulent precipitate, on evaporating a solution of cream of tartar with baryta-water.—*Sodio-baric tartrate*, $C^8H^8Ba''Na^2O^{12}.2H^2O$, is precipitated on mixing a solution of Rochelle-salt with chloride of barium; if, however, the solutions are dilute, it separates, after some time only, in the form of needles; it lightly soluble in water, more soluble in solution of Rochelle-salt.

Tartrate of Cadmium forms woolly needles, nearly insoluble in water.

Tartrates of Calcium.—The *neutral salt*, $C^4H^4Ca''O^6.4H^2O$, exists in several plants, especially in grapes, and is sometimes found in small crystals in the tartar deposited from the juice. It is precipitated, as a white crystalline powder, on mixing tartrate of potassium with a solution of calcic chloride; if the liquors are dilute, the precipitate does not appear for some minutes. Tartaric acid forms, with lime-water, copious white flocks, which gradually become crystalline; the precipitate redissolves in excess of tartaric acid; and the solution, when left at rest, deposits crystals of neutral calcic tartrate. The hard shining crystals of this salt are right rhomboïdal prisms, ∞P, having the basal summits modified by the octahedral face P. Angle $\infty P : \infty P = 97° 30'$; $P : P = 122° 15'$. (Pasteur.)

Tartrate of calcium is very slightly soluble in cold, rather more soluble in boiling water. According to F. Mohr (Jahresb. 1865, p. 393), it requires for solution 6,265 pts. of water at 15°, and 352 pts. of boiling water. Mineral acids, acetic acid, and cream of tartar dissolve it easily. The solutions, unless very concentrated, are not immediately precipitated by ammonia, but the mixture, after some time, deposits crystals of neutral calcic tartrate. The flocculent precipitate formed in a solution of calcic chloride by neutral potassic tartrate, dissolves in sal-ammoniac, and the liquid gradually deposits crystals of calcic tartrate.

Crude tartar containing tartrate of calcium, when kept in a moist warm place, often passes into a state of fermentation, induced by vegetable organisms present in it, the tartaric acid being converted into butyracetic acid. This change is especially liable to take place during the preparation of tartaric acid in warm weather, after the crude tartar has been mixed with lime.

Acid tartrate of Calcium, $C^8H^{10}Ca''O^{12}$, or $C^4H^4Cu''O^6.C^4H^6O^6$, appears to exist in the juice of *Rhus Typhinum*, and is produced (according to Dulk) on adding tartaric acid to lime-water till the precipitate redissolves: the solution, if left to itself, deposits crystals of neutral calcic tartrate, but if evaporated immediately, it yields rhomboïdal octahedrons of the acid tartrate, having the angles of the terminal edges = 82° 50′ and 153°. The crystals are transparent, redden litmus, are slightly soluble in cold water, more soluble in boiling water.

Potassio-calcic tartrate appears to be obtained, in the crystalline state, by spontaneous evaporation of a mixture of cream of tartar and lime-water. Neutral tartrate of calcium dissolves at a gentle heat in caustic potash, and the saturated solution deposits part of the neutral salt on addition of water. When boiled, it is converted into a thick pasty mass, but becomes clear again on cooling. Tartrate of calcium dissolves when boiled with solution of neutral potassic tartrate, and the liquid, evaporated to a syrupy consistence, solidifies on cooling to a mass of needles.

Sodio-calcic tartrate is precipitated in flocks, on mixing a solution of Rochelle-salt with chloride of calcium; if the solutions are dilute, it is gradually deposited in small needles. It is slightly soluble in water, more soluble in excess of Rochelle-salt, still more in chloride of calcium.

Caustic soda reacts with tartrate of calcium like caustic potash.

Tartrate of Cobalt is a red crystallisable salt.—*Potassio-cobaltous tartrate* forms large rhomboïdal prisms.

Tartrates of Copper.—*Cupric tartrate*, $C^4H^4Cu''O^6.3H^2O$, is a light-green crystalline powder, precipitated on mixing the neutral potassium-salt with cupric sulphate or nitrate. It dissolves in 1,715 pts. of cold water, and in 310 pts. of boiling water; also in nitric acid, but is insoluble in tartaric acid.

Potassio-cupric tartrate is obtained in blue crystals by boiling cupric oxide or carbonate with cream of tartar. Cupric tartrate dissolves in caustic potash, forming a blue liquid. Cupric salts mixed with tartaric acid are not precipitated by alkalis.

A solution of cupric sulphate mixed with potash, and a sufficient quantity of tartaric acid to prevent precipitation, is reduced by boiling with many organic substances, especially glucose, and is used for the estimation of the latter (ii. 860).

When a solution of potassio-cupric tartrate is exposed to the action of chlorine, or mixed with an alkaline hypochlorite, not in excess, a yellow precipitate is formed, consisting of a compound of 2 at. cuprous formate ($CHCu'O^2$) with 1 at. sodic carbonate (CNa^2O^3); afterwards cuprous oxide is separated. (E. Millon, Compt. rend. lv. 513; Jahresb. 1862, p. 216.)

A basic *sodio-cupric tartrate*, $C^8H^8Na^2Cu''O^{12}.2CuO.7H^2O$ (?), is obtained by dissolving cupric tartrate in a boiling solution of sodic carbonate; the blue liquid, when concentrated, deposits the double salt in mammellated groups of small tabular crystals, very soluble in water. If the boiling be too much prolonged, a precipitate of cuprous oxide is formed.

Ammoniacal Cupric Tartrates.—The *tetrammoniated salt*, $4NH^3.C^4H^4Cu''O^6$, or *tartrate of ammocuprammonium*, $C^4H^4[N^2H^4(NH^4)^2Cu'']''O^6$, remains, on evaporating a solution of cupric tartrate in ammonia, as an uncrystallisable, hard, vitreous mass, permanent in the air. Its aqueous solution is also very permanent, does not act upon cellulose, and is not reduced by heating with glucose. At 150° it gives off all its ammonia; between 100° and 110° only half, leaving *tartrate of cuprammonium*, $2NH^3.C^4H^4Cu''O^6 = C^4H^4(N^2H^6Cu'')''O^6$.

Cupric tartrate dissolves easily also in aqueous *ethylamine*, forming a dark-blue liquid, which, on evaporation, leaves a blue, vitreous, deliquescent salt, approximating in composition to the formula $C^4H^4\left[\begin{matrix}NH^3\\ NH^2(C^2H^5)\end{matrix}\right\}Cu''\Big]\overset{''}{O}{}^6$. (Schiff, Jahresb. 1862, p. 204.)

Tartrate, Ferrous.—White or pale-green crystalline powder, precipitated on mixing a solution of ferrous sulphate with tartaric acid or neutral potassic tartrate, or on dissolving metallic iron in tartaric acid. It dissolves easily in caustic alkalis, forming a solution which oxidises quickly on exposure to the air.

Tartrates of Lead.—The *monoplumbic* or *dibasic salt*, $C^4H^4Pb''O^6$, is a white crystalline precipitate, obtained by mixing nitrate or acetate of lead with tartaric acid. It is very soluble in nitric acid and in excess of tartaric acid; also in tartrate of ammonium, the concentrated solution solidifying to a gelatinous mass. When treated with chloride of acetyl, it yields chloride of lead and a thick yellowish syrup, which decomposes at 130°, with evolution of carbonic oxide and carbonic anhydride. (Schützenberger, Jahresb. 1861, p. 439.)

A *diplumbic* or *tetrabasic salt*, $C^4H^2\overset{''}{Pb}{}^2O^6$, is obtained by boiling an ammoniacal solution of the monoplumbic salt. (Erdmann, Ann. Ch. Pharm. xxi. 19.—Heintz, Zeitschr. Ch. Pharm. 1861, p. 17.)

Tartrates of Magnesium.—The *neutral salt*, $C^4H^4Mg''O^6.4H^2O$, is obtained in crystalline crusts, by evaporating a solution of magnesium-carbonate in tartaric acid. It dissolves in 122 pts. of water at 16°.—The *acid salt*, $C^8H^{10}Mg''O^{12}$ (crystallised), is formed in the preparation of the neutral salt when an excess of tartaric acid is used. It forms crystalline crusts, soluble in 52 pts. water at 16°.

Potassio-magnesic tartrate, $C^8H^8Mg''K^2O^6.4H^2O$, is obtained, in crystals, by boiling cream of tartar with water and carbonate of magnesium.—An *ammonio-magnesic salt* of corresponding composition is obtained in a similar manner.—The *sodio-magnesic salt*, $C^8H^8Mg''Na^2O^6.5H^2O$, is deposited, on evaporating a mixture of Rochelle-salt and carbonate of magnesium, in monoclinic prisms having the angles $\infty P : \infty P = 129°$; $oP : \infty P\infty = 103°$. Ammonia throws down from the solution of either of these salts a basic tartrate of magnesium, $C^4H^4Mg''O^6.Mg''O.2H^2O$, the formation of which interferes considerably with the use of tartaric acid in Otto's method of separating phosphoric acid from certain bases: hence citric acid is preferable for this purpose. (See Phosphoric Acid, iv. 547.)

Tartrate of Manganese.—A solution of neutral potassic tartrate, mixed with manganous chloride, first deposits acid tartrate of potassium, and then colourless crystals of manganous tartrate, which are decomposed by boiling water into a soluble acid salt and an insoluble basic salt. By dissolving manganous carbonate in cream of tartar, a very soluble salt is obtained, difficult to crystallise.

Tartrate, Mercuric.—White precipitate, insoluble in water, very soluble in weak nitric acid.

Ammonio-mercuric tartrate, obtained by boiling acid tartrate of ammonium with mercuric oxide, forms small prisms soluble in water.—*Tartrate of mercurammonium* is obtained, by digesting mercuric tartrate with ammonia, as a white powder insoluble in water. It appears also to be formed when mercuric oxide is heated with neutral tartrate of ammonium: the oxide then dissolves, with evolution of ammonia; and if an excess of it be used, a white compound separates; the filtered liquid, when concentrated, deposits needles, and, on addition of water, a white precipitate, containing $C^8H^{10}(N^2H^2\overset{''}{Hg}{}^3)''O^{12}.6H^2O$. (Harff, Brandes' Arch. v. 259.—Burckhardt, *ibid.* [2] xi. 257.)

Potassio-mercuric tartrate is obtained, in small slightly soluble prisms, by digesting mercuric oxide with cream of tartar.—When cream of tartar is boiled with chloride of mercurammonium (white precipitate), a large quantity of carbonic anhydride is evolved; the filtered liquid deposits, on evaporation, sparingly soluble salts containing mercury; and the mother-liquors yield needles, apparently consisting of the compound $4C^4H^5KO^6.Hg''Cl^2.6H^2O$.

Tartrate of Nickel.—Precipitated as a green crystalline powder, nearly insoluble in water, on saturating a boiling solution of tartaric acid with hydrate or carbonate of nickel. It dissolves easily in a hot solution of caustic potash or soda, or in sodic carbonate, the solution solidifying to a pasty mass on cooling. Nickel-salts mixed with tartaric acid are not precipitated by alkalis.

Tartrate of Nickel and Potassium, $C^8H^8Ni''K^2O^{12}$ (at 110°), is produced by heating carbonate of nickel with finely-pulverised cream of tartar and water. The resulting green solution is decomposed by boiling, but, when evaporated over oil of vitriol, it yields an apple-green crystalline powder, which effloresces in the air, and dissolves completely in water.

TARTRATE OF PALLADIUM.—Light-yellow precipitate, formed on mixing nitrate of palladium with an alkaline tartrate.

TARTRATES OF STRONTIUM.—The *neutral salt*, $C^4H^4Sr''O^6.4H^2O$, is deposited, on mixing a cold solution of potassic tartrate with nitrate of strontium, in monoclinic prisms, having the angle $oP : \infty P = 92° 35'$; $\infty P : \infty P = 125° 20'$ (De la Provostaye). It dissolves in 147 pts. of water at 16°, and is moderately soluble in solution of sal-ammoniac.—According to Marignac (Ann. Min. [5], xv. 280; Jahresb. 1859, p. 286), a solution of strontium-carbonate in excess of hot aqueous tartaric acid deposits the neutral salt on cooling in trihydrated crystals, $C^4H^4Sr''O^6.3H^2O$, having the form of monoclinic prisms, $\infty P\infty \,.\, [\infty P\infty] \,.\, oP \,.\, +P\infty \,.\, -P\infty$, in which ∞P occurs with only two faces, situated to the right when the crystal is placed with the clinodiagonal directed towards the observer, and the obtuse angle of the inclined axis to the front and above; also a face of $+P$ and a face of $-P$ to the left. Angle $\infty P\infty : \infty P = 140° 1'$; $oP : \infty P\infty = 102°$; $\infty P\infty : +P\infty = 123° 43'$; $\infty P\infty : -P\infty = 137° 32'$; $oP : +P = 128° 4'$; $oP : -P = 138° 20'$. The crystals do not give off any water at 100°.

Tartrate of Strontium and Ammonium, $C^8H^8Sr''(NH^4)^2O^6.12H^2O$, separates from the mother-liquor of the neutral strontium-salt, on neutralisation with ammonia, in thin rectangular laminæ, which are trimetric combinations, $\infty\breve{P}\infty \,.\, \infty P \,.\, \infty\breve{P}2 \,.\, \breve{P}\infty$, with four P-faces occurring hemihedrally. Angle $\infty\breve{P}\infty : \infty P = 124° 58'$; $\infty\breve{P}\infty : \breve{P}\infty = 124° 20'$; $\infty P : P = 140°$. (Marignac, *loc. cit.*).

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TARTRATE OF TIN. STANNOUS TARTRATE, $C^4H^4Sn''O^6$.—Prepared by pouring a boiling solution of tartaric acid into a concentrated solution of stannous acetate. It forms white microscopic crystals, consisting of prisms with rectangular base, soluble in cold water, more soluble and without decomposition in boiling water, still more in water acidulated with tartaric acid, the solution not being precipitated by ammonia. When strongly heated, it leaves a residue of stannic oxide.

By treating the acid tartrates of ammonium and potassium with stannous oxide, salts are formed which crystallise well, and appear to be perfectly stable in presence of water.

TARTRATE, URANOUS.—Tartaric acid throws down from uranous chloride a greyish-green precipitate, consisting of a basic salt, $2C^4H^4U''O^6.U''H^2O^2$, which is very soluble in hydrochloric acid, and is not precipitated by ammonia.

TARTRATES OF YTTRIUM.—The *neutral salt*, $C^4H^4Y''O^6.4H^2O$, is formed, on adding neutral tartrate of potassium to acetate of yttrium, as a bulky precipitate soluble in excess of the potassium-salt. Its solution in an equivalent quantity of tartaric acid deposits after a while a crystalline precipitate, insoluble in water, consisting of the *acid salt*, $C^8H^{10}Y''O^{12}$. (Popp, Jahresb. 1864, p. 205.)

TARTRATE OF ZINC.—Hot concentrated solutions of zinc-sulphate and neutral potassic tartrate, yield a yellowish-white crystalline precipitate, very slightly soluble in water, easily soluble in caustic potash or soda. Cream of tartar digested with excess of zinc or its oxide, forms a solution which deposits a white powder, and dries up to a gummy mass.

γ. *Tartrates containing Triatomic Metals and Metalloïds.*

TARTRATE OF ALUMINIUM.—This salt occurs in *Lycopodium clavatum*. Its solution, when evaporated, leaves a gummy non-deliquescent mass.

The solution of neutral potassic tartrate dissolves a large quantity of alumina without becoming alkaline; the liquid, on addition of alcohol, deposits oily drops, the aqueous solution of which dries up by evaporation to a gummy mass, containing both potash and alumina. Acid tartrate of potassium likewise dissolves alumina, forming an amorphous mass, which is not precipitated by alkalis.

TARTRATES OF ANTIMONY. (Respecting the several views of the constitution of these salts, see p. 676).—*Neutral antimonious tartrate*, $C^4H^4(SbO)^2O^6.H^2O$, is the

Ammoniacal Cupric Tartrates.—The *tetrammoniated salt*, $4NH^3.C^4H^4Cu''O^6$, or *tartrate of ammocuprammonium*, $C^4H^4[N^2H^4(NH^4)^2Cu'']''O^6$, remains, on evaporating a solution of cupric tartrate in ammonia, as an uncrystallisable, hard, vitreous mass, permanent in the air. Its aqueous solution is also very permanent, does not act upon cellulose, and is not reduced by heating with glucose. At 150° it gives off all its ammonia; between 100° and 110° only half, leaving *tartrate of cuprammonium*, $2NH^3.C^4H^4Cu''O^6 = C^4H^4(N^2H^6Cu'')''O^6$.

Cupric tartrate dissolves easily also in aqueous *ethylamine*, forming a dark-blue liquid, which, on evaporation, leaves a blue, vitreous, deliquescent salt, approximating in composition to the formula $C^4H^4\left[\left.\begin{matrix}NH^3\\NH^2(C^2H^5)\end{matrix}\right\}Cu''\right]\overset{''}{O}{}^6$. (**Schiff**, Jahresb. 1862, p. 204.)

Tartrate, Ferrous.—White or pale-green crystalline powder, precipitated on mixing a solution of ferrous sulphate with tartaric acid or neutral potassic tartrate, or on dissolving metallic iron in tartaric acid. It dissolves easily in caustic alkalis, forming a solution which oxidises quickly on exposure to the air.

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TARTRATES OF ANTIMONY. (Respecting the several views of the constitution of these salts, see p. 676).—*Neutral antimonious tartrate*, $C^4H^4(SbO)^2O^6.H^2O$, is the white granular precipitate formed on adding alcohol to a solution of antimonious oxide in aqueous tartaric acid. It is insoluble in water, gives off its water of crystallisation at 100°, and an additional atom of water at 190°, leaving the salt $C^4H^2(SbO)''O^5$, analogous in composition to the first anhydride of tartaric acid.—*Acid antimonious tartrate*, $C^4H^5(SbO)O^6$, or $C^4H^4(SbO)^2O^6.C^4H^6O^6$ (?), appears to be formed on adding alcohol to the concentrated solution of the hyperacid salt. At 160° it gives off 1 at. water, leaving the salt $C^4H^3(SbO)O^5$.—The *hyperacid salt*, $C^4H^4(SbO)^2O^6.3C^4H^6O^6.5H^2O$, is deposited, after some time, from a syrupy solution of antimonious oxide in excess of tartaric acid, in large crystals derived from a right rectangular prism. It is very soluble in water, deliquesces in moist air, and gives off 23·1 per cent. water at 160°. (Péligot, Ann. Ch. Phys. [3] xx. 289.)

Ammonio-antimonious tartrate, $C^4H^4(NH^4)(SbO)O^6.\frac{1}{2}H^2O$, is produced by boiling antimonious oxide with solution of acid tartrate of ammonium. The filtered solution, evaporated to a stiff jelly, gradually yields rather large octahedral crystals belonging to the trimetric system, in which the axes $a : b : c = 0·8923 : 1 : 1·0801$. Angle P : P (brach.) = 110° 58′; P : P (macr.) = 101° 8′; P : P (basal) = 116° 42′. Ordinary combination, P . oP . 2P . ∞P, the P-faces being predominant, and four of them, so situated as to form by extension a rhombic sphenoïd, being more developed than the other four. Cleavage parallel to oP. The crystals are isomorphous with those of ordinary tartar-emetic, and more soluble than the latter. They effloresce on exposure to the air, and give off ammonia when heated a little above 100°.

When the octahedral crystals just described have been removed from the mother-liquor, this liquid yields, in a short time, fine prismatic crystals, much more efflorescent than the octahedral crystals, and containing $\frac{5}{2}$ at. water (15·3 per cent.), which they give off at 100°. These crystals are rhombic prisms, having the angle ∞P : ∞P = 127°, and hemihedral from having two only of the edges of each base replaced by the octahedral faces $\frac{P}{2}$, forming an angle of 85° 30′, and situated alternately on the two bases. (Pasteur.)

Potassio-antimonious tartrate, $C^4H^4K(SbO)O^6.\frac{1}{2}H^2O$. *Tartar-emetic. Tartarus emeticus. Tartarus stibiatus. Brechweinstein. Spiessglanzweinstein.*—This salt was known to the older chemists. It is generally said to have been discovered by Mynsicht (about 1631), but it had been previously mentioned by Basil Valentine, about the end of the fifteenth century. It is prepared by boiling 3 pts. antimonious oxide for about half an hour with 4 pts. cream of tartar, renewing the water as it evaporates, and filtering the solution while still hot. Instead of antimonious oxide, the oxychloride (algaroth-powder) or oxysulphide (glass of antimony) may be used.

Potassio-antimonious tartrate forms octahedral crystals isomorphous with the corresponding ammonium-salt, and exhibiting the same faces and direction of cleavage. Axes $a : b : c = 0·9556 : 1 : 1·054$. Angle P : P (brach.) = 108° 16′; P : P (macr.) = 104° 22′; P : P (basal) = 116°. Optical rotatory power $[\alpha]^j = +156° 2′$. Specific gravity of the crystals = 2·607 (Schiff); 2·588 (Buignet).

Tartar-emetic gives off part of its water of crystallisation on exposure to the air, the crystals then becoming opaque, and the whole at 100°. When heated to 200°, it gives off another atom of water, and leaves the salt $C^4H^2K(SbO)O^5$, analogous in constitution to the first anhydride of tartaric acid.

Tartar-emetic dissolves in 14·5 pts. of cold and 1·9 pt. of boiling water. The solution yields a crystalline precipitate with alcohol, reddens litmus, and has a nauseous metallic taste. It is used in medicine; from 5 to 10 centigrammes are sufficient to excite vomiting; in large doses it is poisonous. It is also used externally as an ingredient of pommades and plasters for the treatment of skin-diseases, chronic catarrh, &c.

Sulphuric, *hydrochloric*, and *nitric acids* form, with solution of tartar-emetic, white precipitates consisting of basic antimony-salts, soluble in excess of those acids, and in tartaric acid.—*Ammonia* forms, in the concentrated aqueous solution, a white precipitate of antimonious oxide insoluble in excess of ammonia.—*Potash* forms a similar precipitate, soluble in excess.—*Mercuric chloride* forms a precipitate of calomel.—*Sulphydric acid* throws down orange-red antimonious sulphide; *infusion of galls* throws down white flocks, and produces a cloud even in dilute solutions.

Tartar-emetic is reduced at a white heat, yielding an alloy of antimony and potassium, mixed with charcoal, which decomposes water with evolution of hydrogen, and, when brought in contact with a few drops of water, sometimes produces violent explosions.

An *acid potassio-antimonious tartrate*, $C^4H^4K(SbO)O^6.C^4H^6O^6.\frac{5}{2}H^2O$, is usually contained in the mother-liquors of ordinary tartar-emetic, and is likewise produced by mixing 9 pts. of the latter with 4 pts. of tartaric acid, and evaporating at a gentle heat. The solution first deposits crystals of common tartar-emetic, then (when it has attained a syrupy consistence) confused crystals of the acid salt, having the form of oblique rhomboïdal prisms, which effloresce on exposure to the air, and give off 9·22 per cent. water at 100°. Alcohol, added to the solution of this salt, throws down tartar-emetic, leaving tartaric acid in solution. (Knapp, Ann. Ch. Pharm. xxxii. 76.)

A compound of *tartar-emetic and cream of tartar*, $C^4H^4K(SbO)O^6.3C^4H^5KO^6$, is obtained by boiling equal weights of the two salts with water. On adding carbonate of potassium to the solution as long as effervescence takes place, and evaporating, mammellated groups of needles are obtained, resembling wavellite in appearance, and probably consisting of a compound of tartar-emetic with neutral tartrate of potassium. They are very soluble in water, and tartaric acid added to the solution throws down scales of the preceding salt. (Knapp.)

Potassio-antimonic tartrate, probably $C^8H^4K(SbO^2)O^6.\,xH^2O$, is prepared, like tartar-emetic, with antimonic oxide and cream of tartar. The solution, which is not precipitated by hydrochloric acid, dries up on evaporation to a gummy mass. (Geiger and Reimann, Mag. Pharm. xvii. 18.—Mitscherlich, Pogg. Ann. lxxiii. 396.)

Rubidio-antimonious tartrate, $C^4H^4Rb(SbO)O^6.\frac{1}{2}H^2O$.—Prepared like tartar-emetic. The solution, filtered at the boiling heat, first deposits crystalline crusts containing but little antimony (probably impure acid tartrate of rubidium), and, when further concentrated and left to itself, crystals of the double salt, isomorphous with tartar-emetic. (Grandeau, Ann. Ch. Phys. [3] lxvii. 155.)

Sodio-antimonious tartrate, $C^4H^4Na(SbO)O^6.\frac{1}{2}H^2O$, is prepared in the same manner as the potassium-salt. The crystals, which absorb moisture from the air, are trimetric, having the axes $a : b : c = 0·9217 : 1 : 1·08$. Angle $\infty P : \infty P = 85° 20'$; $\infty P : \infty\breve{P}\infty = 137° 20'$. Ordinary combination $\infty P \,.\, \infty\breve{P}\infty \,.\, \infty\bar{P}\infty \,.\, oP \,.\, \bar{P}\infty \,.\, \frac{1}{2}P\infty$.

Double Salts, analogous to Tartar-emetic, obtained by Precipitation.—The solution of tartar-emetic forms, with salts of barium, calcium, strontium, cadmium, lead, and silver, precipitates consisting of tartar-emetic in which the potassium is replaced by the other metal.—The *argentic salt* has the composition $C^4H^4Ag(SbO)O^6$.—The other salts are represented by the general formula $C^8H^8M''(SbO)^2O^{12}$.—The *barium-salt* is precipitated in white scales, containing 2 at. water, which they give off at 150°.—The *cadmium-salt*, $C^8H^8Cd''(SbO)^2O^{12}$ (at 100°), gives off 2 at. water at 200°, leaving the salt $C^8H^4Cd''(SbO)^2O^{10}$ (Schiff, Jahresb. 1857, p. 221).—A compound of *calcio-antimonious tartrate with calcic nitrate*, $4C^8H^8Ca''(SbO)^2O^{12}.Ca''N^2O^6.6H^2O$, crystallises from a solution of tartar-emetic mixed with excess of calcic nitrate, in trimetric combinations $oP \,.\, \infty\breve{P}\infty \,.\, \infty P \,.\, \breve{P}\infty \,.\, \frac{1}{2}\breve{P}\infty \,.\, \bar{P}\infty \,.\, \frac{P}{2}$ (sphenoïdally hemihedral), which, when oP and $\infty\breve{P}\infty$ are predominant, and ∞P and $\bar{P}\infty$ equally developed, present the appearance of quadratic forms with the faces ∞P and P predominating. Angle $\infty P : \infty P$ (brach.) $= 124° 6'$; $\bar{P}\infty : \bar{P}\infty$ (basal) $= 124° 40'$; $oP : \breve{P}\infty = 134° 39'$. The compound, when recrystallised, is partially decomposed, with separation of pulverulent calcio-antimonious tartrate (Marignac, Ann. Min. [5] xv. 280; Jahresb. 1859, p. 287).—*Strontio-antimonious tartrate*, $C^8H^8Sr''(SbO)^2O^{12}$, first prepared by Kessler, is obtained by dissolving pulverised tartar-emetic in a cold solution of excess of strontium-nitrate; and separates, on warming the liquid, in hexagonal combinations of ∞P with P, $2P$ or oP. Angle $P : P$ (terminal) $= 138° 26'$; $2P : 2P$ (terminal) $= 126° 48'$; $\infty P : P = 135° 12'$; $\infty P : 2P = 153° 36'$ (Marignac, *loc. cit.*). By digesting 1 pt. of strontium-nitrate with 2 pts. water and an excess of strontio-antimonious tartrate at 30°—35°, and leaving the filtrate to evaporate, large very soluble crystals are obtained, consisting of the compound $C^8H^8Sr''(SbO)^2O^{12}.Sr''N^2O^6.H^2O$, the solution of which deposits strontio-antimonious tartrate on boiling. (Kessler, Pogg. Ann. lxxv. 410.)

Double Salts of Antimonious Tartrate containing Organic Bases.—These salts are prepared by boiling the acid tartrates of the several bases with antimonious oxide, or the bases themselves with tartar-emetic.—The *berberine-salt*, $C^4H^4(C^{20}H^{18}NO^4)(SbO)O^6$, crystallises like wavellite, is very slightly soluble in cold water, and may be recrystallised without decomposition from alcohol (Stenhouse, Jahresb. 1863, p. 452).—The *brucine-salt*, $C^4H^4(C^{23}H^{27}N^2O)(SbO)O^6$, forms short very brittle crystals (Stenhouse, *ibid.* p. 447).—The *cinchonidine-salt* crystallises in prisms easily soluble in water and in alcohol (Hesse, *ibid.* 1865, p. 445).—The *morphine-salt* forms nodular groups of crystals, sparingly soluble in cold water, and decomposed by prolonged boiling with water (Decharme, *ibid.* 1853, p. 445).—The *strychnine-salt* forms brittle needles or laminæ, very slightly soluble in water. (Stenhouse.)

TARTRATES OF ARSENIC.—Arsenious and arsenic oxide dissolve in acid tartrates of alkali-metal, forming double salts analogous to tartar-emetic. (Mitscherlich, *Lehrbuch.*—Pelouze, Ann. Ch. Phys. [3] vi. 63.—Marignac, *loc. cit.*)

Ammonio-arsenious tartrate, $C^4H^4(NH^4)(AsO)O^6.\frac{1}{2}H^2O$, is prepared by boiling arsenious oxide for a long time with acid tartrate of ammonium, the filtered liquid first depositing crusts of the latter salt with a little arsenious oxide, and afterwards, when strongly concentrated, large efflorescent crystals of the double salt, which are trimetric combinations having the axes $a : b : c = 0{\cdot}8760 : 1 : 0{\cdot}6941$. Angle $P : P$ (brach.) = 122° 54′; $P : P$ (macr.) = 113° 52′; $P : P$ (basal) = 93°; $\infty P : \infty P$ (macr.) = 82° 26′; $2\breve{P}\infty : 2\breve{P}\infty$ (basal) = 108° 28′. Observed combination $\infty P . \infty\breve{P}\infty . P . 2\breve{P}\infty . oP$ (Marignac).—The corresponding *potassium-* and *sodium-salts* are obtained in like manner, but do not crystallise so well. Marignac obtained the potassium-salt in rhombic prisms of 92° 50′ with dihedral summits of 85° 10′, resting on the acute prismatic edges.

Potassio-arsenic tartrate, $C^4H^4K(AsO^2)O^6.\frac{5}{2}H^2O$, is obtained by adding 1 pt. of cream of tartar to a solution of rather more than 1 pt. arsenic oxide (As^2O^5) in 5 or 6 pts. of water, and raising the liquid to the boiling heat—or, better, mixing it with alcohol, the double salt then separating as a crystalline powder. It is very soluble in water, which however quickly decomposes it, liberating acid tartrate of potassium. It parts with its water of crystallisation at 100°, but does not give off any more water at higher temperatures without undergoing complete decomposition. (Pelouze.)

A compound of *strontio-arsenious tartrate* with *nitrate of ammonium*, $2C^8H^8Sr''(AsO)^2O^{12}.(NH^4)NO^3.12H^2O$, separates from a mixture of the component salts in large trimetric crystals, $\infty P . \infty\bar{P}2 . \infty\bar{P}\infty . \infty\breve{P}\infty . \breve{P}\infty . \frac{1}{2}\breve{P}\infty$. Angle $\infty P : \infty P$ (brach.) = 113° 58′; $\breve{P}\infty : \breve{P}\infty$ (brach.) = 113°. The form of the crystals resembles that of a dimetric or quadratic combination, in which $\infty\breve{P}\infty$ would form the end-face; but the crystals are not optically uniaxial. (Marignac.)

TARTRATES OF BISMUTH, $C^{12}H^{12}Bi^2O^{18}.6H^2O = Bi^2O^3.3C^4H^4O^5.6H^2O$.—When a hot concentrated solution of 4 pts. tartaric acid is added to a hot, moderately strong solution of 5 pts. bismuth-oxide in nitric acid, the mixture first remains limpid, but, when left at rest, deposits a considerable quantity of bismuth-tartrate in small crystals, forming a hard white crust at the bottom of the liquid; they must be washed with aqueous tartaric acid, as pure water decomposes them. (R. Schneider, Pogg. Ann. lxxxviii. 55.)

Tartrate of Bismuth and Potassium is produced by boiling a solution of cream of tartar with excess of bismuth-oxide, and is deposited, on concentrating the liquid, as a perfectly white powder, containing (at 100°) $C^4H^2K(BiO)O^5$, analogous therefore to tartar-emetic dried at 200°. (Schwarzenberg, Ann. Ch. Pharm. lxi. 244.)

TARTRATES OF BORON. (Meyrac, J. Pharm. iii. 8.—Soubeiran, *ibid.* iii. 399; xi. 560; xxxv. 241.—Soubeiran and Capitaine, *ibid.* xxv. 741.—Duflos, Schw. J. lxiv. 333.—Vogel, J. Pharm. iii. 1.—Robiquet, *ibid.* [3] xxi. 197.—Wackenroder, Arch. Pharm. [2] lviii. 4.—Wittstein, Repert. Pharm. [3] vi. 1, 177.—*On the optical characters of these salts:* Biot, Ann. Ch. Phys. [3] xi. 82.)—Tartaric acid forms, with boron and the alkali-metals, salts analogous to tartar-emetic, the group BO taking the place of hydrogen, or a metal, just like the group SbO.

Tartaric and boric acids, triturated together, form a mixture which appears to be a definite compound, inasmuch as it deliquesces in moist air—a property not exhibited either by tartaric or by boric acid alone. Boric acid also dissolves in water containing tartaric acid more easily than in pure water, the boric acid being, however, deposited on evaporation.

Boropotassic tartrate, $C^4H^4K(BO)O^6$ (at 100°)—also called *Borotartrate of potassium*, or *Soluble Cream of Tartar*—is obtained by evaporating to dryness, 1 pt. boric anhydride, 2 pts. cream of tartar, and 24 pts. of water, and treating the mass with alcohol, which takes up the excess of boric acid. It is a white amorphous mass, very soluble in water, but insoluble in alcohol. Mineral acids added to its solution, do not throw down either boric acid or cream of tartar. At 180° it gives off 1 at. water, leaving the salt $C^4H^2K(BO)O^5$, and behaves in other respects like tartar-emetic. Soluble cream of tartar is used in medicine as a purgative, and externally as a lotion for ulcers.

By boiling, for some hours, 1 pt. boric acid and 12 pts. cream of tartar with a large quantity of water, removing the deposit of cream of tartar which settles down on cooling, then evaporating to dryness, taking up the residue with a little cold water, removing the new deposit of cream of tartar (if any), repeating these operations till cold water no longer separates the latter salt, and finally treating the product with boiling alcohol, a salt is obtained, containing 11·4 per cent. of boric anhydride (B^2O^3), and apparently consisting of a compound of potassio-boric tartrate with cream of tartar, $C^4H^4K(BO)O^6.C^4H^5KO^6$.

Sodio-boric tartrate appears to be obtained in the same manner as the potassium-salt. Acid tartrate of sodium forms a gummy deliquescent salt with borax, also with borate of ammonium; 1 pt. borax and 3 pts. cream of tartar, dissolved together, yield on evaporation a gummy deliquescent salt, called *tartarised borax*, containing (according to Duflos and Vogel) 3·6 per cent. borax, and agreeing with the formula $2C^4H^4K(BO)O^6.C^4H^4Na(BO)O^6.6H^2O$.

Calcio-boric tartrate is formed, in combination with tartrate of calcium, by precipitating a solution of cream of tartar neutralised with ammonia, with chloride of calcium.

TARTRATES OF CHROMIUM.—The solution of chromic hydrate in tartaric acid dries up to a violet mass, probably consisting of neutral chromic tartrate.

Potassio-chromic tartrate, or *Chromotartrate of potassium*, $C^4H^4K(CrO)O^6 . \frac{1}{2}H^2O$, is formed on adding pulverised tartaric acid to a hot aqueous solution of potassic dichromate, as long as carbonic acid continues to be evolved; it is precipitated by alcohol from its dark-green aqueous solution. The same solution, mixed with a strong solution of neutral potassic tartrate, deposits dark-green crystalline grains, containing 1 at. potash (K^2O) to 3 at. chromic oxide. Potassio-chromic tartrate forms, with acetate of lead, a bluish-green precipitate, which, when, decomposed by sulphuretted hydrogen, yields a tartrate of chromium, probably consisting of chromotartaric acid, $C^4H^3(CrO)O^6$. (Berlin, *Berz. Lehrbuch.*—Malaguti, Compt. rend. xvi. 457.—Lœwel, *ibid.* xvi. 862.)

TARTRATES OF IRON (*ferricum*).—Tartaric acid dissolves recently precipitated ferric hydrate, and the solution, evaporated below 50°, yields an amorphous mass, apparently consisting of ferric tartrate. The solution, which is not precipitated by alkalis, probably contains originally normal ferric tartrate, $C^{12}H^{12}\overset{'''}{Fe}{}^2O^{18}$, which is resolved, on evaporation, into a basic and an acid salt, the latter being partly converted, by the prolonged action of warmth and light, into ferrous tartrate, which remains in solution mixed with free tartaric acid; this acid is, however, partially oxidised at the same time. (Ludwig, Jahresb. 1861, p. 434.)

Ammonio-ferric tartrate, $C^4H^4(NH^4)(FeO)O^6 + 4$ to $5H^2O$, is obtained by dissolving recently precipitated ferric hydrate in acid tartrate of ammonium, and evaporating, in garnet-coloured scales, soluble in rather more than 1 pt. of water. The solution is precipitated by alcohol.

Potassio-ferric tartrate, $C^4H^4K(FeO)O^6$ (at 100°).—This salt, which constitutes the essential part of the *Tartarus chalybeatus* or *Mars solubilis*, and the *Globuli martiales* of the pharmacopœias, is prepared by digesting cream of tartar with water and recently precipitated ferric hydrate, or with iron filings in a vessel exposed to the air; in either case, however, the product is frequently contaminated with ferrous salt. Pure potassio-ferric tartrate forms shining scales of a brown or nearly black colour, exhibiting a fine red tint by transmitted light. The salt decomposes at 150°, giving off water and carbonic acid. Acids precipitate from its solution a basic ferric salt, soluble in excess of the acid. (*Gmelin's Handbook*, x. 316.)

Rubidio-ferric tartrate is formed by boiling ferric oxide with acid tartrate of rubidium, and separates on evaporation in right rhombic prisms with hemihedral faces. (Grandeau, Jahresb. 1863, p. 184.)

TARTRATES OF URANYL, OR URANIC TARTRATES. *Neutral Uranic Salt*, $C^4H^4(UO)^2O^6 + H^2O$ and $4H^2O$.—The yellow solution of uranic oxide in tartaric acid yields, by concentration, crystals containing 1 at. water, and by spontaneous evaporation in a vacuum, crystals containing 4 at. water. The last give off 3 at. water at 150°: the salt does not experience any further loss by drying at 200° (Péligot, Ann. Ch. Phys. [3] xii. 463).—Uranic salts are precipitated by alkalis, even when mixed with tartaric acid. (H. Rose.)

Antimonio-uranic tartrate, $C^4H^4(SbO)(UO)O^6.4H^2O$, is obtained, in yellow silky needles, on mixing the aqueous solutions of tartar-emetic and uranic nitrate, and redissolving the gelatinous precipitate in boiling water. This salt, when dried at 100°, exhibits the composition $C^4H^2(SbO)(UO)O^5$, analogous to that of the first anhydride of tartaric acid. (Péligot.)

ACIDS ISOMERIC WITH TARTARIC ACID.

Racemic or Paratartaric Acid has been already described (p. 34).

Inactive Tartaric Acid, or **Mesotartaric Acid.**—This is a modification of tartaric acid, inactive to polarised light, but differing from racemic acid in not being separable into dextro- and lævo-tartaric acids. It is obtained, as above mentioned (p. 672), by heating racemate or tartrate of cinchonine to 170° for several hours. On dissolving the product in water, adding chloride of calcium, filtering immediately from the racemate of calcium which separates out, and leaving the filtrate to itself, the calcium-salt of inactive tartaric acid separates out. The acid crystallises well, and most of its salts are quite equal in beauty to the corresponding tartrates and racemates. (Pasteur, Ann. Ch. Pharm. lxxxviii. 212.)

The inactive tartaric acid prepared from dibromosuccinic acid is probably the same modification.

Mesotartaric acid, obtained by Dessaignes (Compt. rend. lv. 769; Jahresb. 1862, p. 305), together with dextrotartaric, racemic, and aposorbic acids, by oxidising sorbin with nitric acid, also by boiling tartaric or racemic acid for a long time (at least 400 hours) with hydrochloric acid, appears also, from comparative experiments of Pasteur (Bull. Soc. Chim. 1862, p. 107), to be identical with inactive tartaric acid.

a. It is separated from the oxidation-products of sorbin by first removing the tartaric and racemic acid as acid ammonium-salts, precipitating the acid filtrate with chloride of calcium, and decomposing the calcium-salt with sulphuric acid.—*β*. In preparing it from tartaric acid, the greater part of the unaltered tartaric acid, and a certain quantity of racemic acid, likewise formed in the reaction, must first be removed by crystallisation, the hydrochloric acid expelled by evaporation over the water-bath, and the remaining liquid half neutralised with ammonia, whereby nearly all the tartaric acid is precipitated as acid ammonium-salt. The filtrate, when concentrated, yields large well-defined crystals of acid mesotartrate of ammonium.—*γ*. In preparing it from racemic acid, the unaltered racemic acid is removed by crystallisation, the hydrochloric acid expelled by evaporation, the remaining liquid half neutralised with ammonia, and then precipitated with acetate of calcium.

Mesotartaric acid is very soluble in water (10 pts. dissolving in 8 pts. of water at 15°). It usually crystallises in rectangular plates containing 1 at. water of crystallisation: $C^4H^6O^6.H^2O$. These crystals effloresce in a vacuum, and give off their water of crystallisation at 100°. If the residue be then dissolved in water, and the solution evaporated to the crystalline point, large anhydrous crystals are obtained, resembling those of ordinary tartaric acid. The solution of these crystals, however, if left to itself, gradually yields the hydrated acid.

Mesotartaric acid melts at 140°; at 200° it is partly decomposed, giving off pyrotartaric acid; the remaining portion is partly converted into racemic acid. It is also transformed into racemic acid by prolonged boiling with hydrochloric acid. (Dessaignes, Bull. Soc. Chim. 1865, i. 34; Jahresb. 1865, p. 393.)

The mesotartrates for the most part resemble the tartrates, but the acid ammonium- and potassium-salts are moderately soluble in water, and the acid does not precipitate a solution of gypsum.—The *calcium-salt*, $C^4H^4Ca''O^6.4H^2O$, dissolves in hydrochloric acid, and is precipitated from the solution by ammonia; it also reacts with potash in the same way as tartrate of calcium.—The *lead-salt* contains $C^4H^4Pb''O^6.H^2O$; the *silver-salt*, $C^4H^4Ag^2O^6.H^2O$.

Metatartaric Acid. This isomer of tartaric acid, discovered in 1831 by Braconnot (Ann. Ch. Phys. [2] lxviii. 299), and further examined by Erdmann (Ann. Ch. Pharm. xxi. 9), and by Laurent and Gerhardt (*ibid.* lxx. 848), is produced by quickly heating tartaric acid to 170°—180°, and keeping it at that temperature till completely fused. The product is a transparent gummy mass, which gradually becomes opaque and crystalline. If the heat be continued longer, ditartaric acid is also produced.

Metatartaric acid is deliquescent. While still hot and liquid, it turns the plane of polarisation strongly to the right; but as it cools and solidifies, the dextrorotatory power becomes weaker, and at 3·5° perceptible lævorotation is produced.

The metatartrates have the same composition as the tartrates, but are for the most part distinguished from them by their crystalline forms, and by greater solubility. By boiling their aqueous solutions, they are gradually converted into tartrates.

The *acid ammonium-salt*, $C^4H^5(NH^4)O^6$, separates from very concentrated solutions in groups of microscopic needles, usually exhibiting the form of spindles, somewhat thickened in the middle. It is more soluble than the acid tartrate, and is further distinguished therefrom by not giving any precipitate with chloride of calcium. Its solution, saturated with ammonia, is precipitated by chloride of calcium only when highly concentrated; and the crystalline *metatartrate of calcium* thus obtained, $C^4H^4Ca''O^6.4H^2O$, is distinguished from the tartrate by the form of its crystals, which appear, under the microscope, as irregular lenticular grains, or small prisms unsymmetrical at the two ends, whereas the tartrate forms small often elongated octahedrons. Metatartrate of calcium gives off half its water of crystallisation at 160°, and the rest at 230°. When once deposited in the crystalline state, it dissolves but very slowly in boiling water, being at the same time converted into tartrate; but it dissolves easily in cold water, especially if slightly acidulated with nitric or hydrochloric acid. The liquid neutralised with ammonia again, after a while, deposits metatartrate of calcium, with its characteristic crystalline form; but if the metatartrate dried at 220° be dissolved in hydrochloric acid, the solution, neutralised with ammonia, yields octahedral crystals of calcic tartrate. (Laurent and Gerhardt.)

Acid metatartrate of potassium, $C^4H^5KO^6$, resembles the acid tartrate in appearance and in its reactions. On neutralising metatartaric acid with potash, and adding alcohol, a limpid oil is precipitated, which crystallises slowly, in the form of neutral potassic tartrate, and the solution of which yields with calcium-salts octahedral crystals of calcic tartrate.

Glycotartaric Acid, $C^4H^6O^6$. (A. Schöyen, Ann. Ch. Pharm. cxxxii. 168.)—Glyoxal, $C^2H^2O^2$, unites with 2 at. hydrocyanic acid, forming a black amorphous substance, which, when heated with alkalis, gives off ammonia, and is converted into glycotartaric acid. This acid is deliquescent, alterable at 100°, and, when more strongly heated, gives off the same odour as tartaric acid.

The glycotartrates of the *alkali-metals*, even the acid potassium-salt, are easily soluble, and their solutions are precipitated by chloride of barium, chloride of calcium, acetate of lead, and nitrate of silver.—The *barium-salt* contains $C^4H^4Ba''O^6.H^2O$; the *lead-salt*, $C^4H^4Pb''O^6.H^2O$.

Acids derived from Tartaric Acid by substitution of Acid Radicles for the Alcoholic Hydrogen.

Diacetotartaric Acid, $C^8H^{10}O^8 = \left.\begin{matrix}(C^2H^3O)^2\\(C^4H^2O^2)^{iv}\\H^2\end{matrix}\right\}O^4$, and **Diacetotartaric Anhydride,** $C^8H^8O^7 = \left.\begin{matrix}(C^2H^3O)^2\\(C^4H^2O^2)^{iv}\end{matrix}\right\}O^3$. (Ballik, Wien. Akad. Ber. xxix. 26.—Pilz, *ibid.* xliv. [2] 7; Jahresb. 1861, p. 368.—Perkin, Chem. Soc. Qu. J. xx. 149).—The anhydride is produced by heating pulverised tartaric acid with chloride of acetyl:

$$C^4H^6O^6 + 2C^2H^3OCl = C^8H^8O^7 + 2HCl + H^2O.$$

It is a tough crystalline solid, melting at 126°—127° C. When distilled, it undergoes a considerable amount of decomposition, especially if the distillation be carried on slowly. It boils above 250° C, but no fixed point can be obtained, acetic anhydride coming over during the distillation, as well as other products, some of which affect the eyes like acrolein; a residue of carbon is left in the retort. If heated gently, it sublimes in beautiful but small prisms. It is slightly soluble in benzene, and crystallises from this solvent in slender white needles. It also crystallises from acetic anhydride. (Perkin.)

Diacetotartaric acid, $C^8H^{10}O^8 = C^8H^8O^7.H^2O$, is formed by the direct combination of the anhydride with water. The aqueous solution, evaporated in a vacuum, leaves the acid as a transparent, gummy, deliquescent substance, having a very acid taste. When strongly heated, it decomposes, without previous formation of the anhydride. Heated with caustic potash or soda, it is resolved into tartaric and acetic acids:

$$C^8H^{10}O^8 + 2H^2O = C^4H^6O^6 + 2C^2H^4O^2.$$

Diacetotartaric acid is dibasic, forming acid and neutral salts; they are all very soluble, and somewhat difficult to obtain pure; they are prepared by dissolving the several carbonates in the aqueous acid.

The *neutral potassium-* and *sodium-salts* are very deliquescent.—The *acid potassium-salt*, $C^8H^9KO^8$, is a crystalline powder, very soluble, but not deliquescent; it has an acid taste, and reddens litmus powerfully.—The *barium-salt*, $C^8H^8Ba''O^8$, crystallises from a syrupy solution, in slender deliquescent needles, sometimes half an inch long.—The *calcium-salt*, $C^8H^8Ca''O^8$, dries up, on evaporation, to an opaque, friable, deliquescent mass.—The *cupric salt*, $C^8H^8Ca''O^8$, forms blue crystals.—The *mercurous salt* is a gelatinous precipitate, soluble in acetic acid.—The *silver-salt*, $C^8H^8Ag^2O^8$, is a white crystalline mass, very slowly acted upon by light. (Perkin.)

Paratartaric (*racemic*) *acid*, heated with chloride of acetyl, yields diacetoparatartaric anhydride, as a beautiful crystalline body, isomeric with diacetotartaric anhydride, which it resembles in melting-point and other properties. In contact with water, it yields diacetoparatartaric acid, which is resolved by heating with alkalis into acetic and paratartaric acids. (Perkin.)

Benzotartaric Acid, $C^{11}H^{10}O^7 = \left.\begin{matrix}H.C^7H^5O\\(C^4H^2O^2)^{iv}\\H^2\end{matrix}\right\}O^4$. (Dessaignes, J. Pharm. [3]

xxxii. 47; Jahresb. 1847, p. 307.)—Produced by heating 1 at. tartaric acid and 1 at. benzoic acid to 150° in a sealed tube:

$$C^4H^6O^6 + C^7H^6O^2 = H^2O + C^{11}H^{10}O^7.$$

A brown liquid is thereby formed, which, when dissolved in hot water, deposits benzoic acid; the residue, left on evaporating the mother-liquor to dryness, dissolves partially in carbonate of sodium; and the solution, decolorised with charcoal and slightly supersaturated with hydrochloric acid, deposits benzotartaric acid, in warty groups of microscopic crystals (Dessaignes). It is also formed, together with ethylbenzotartaric acid, by the action of dilute alcoholic potash on benzotartaric ether, and remains in the mother-liquor after the ethylbenzotartaric acid has separated out. (Perkin, p. 695.)

Benzotartaric acid is more soluble than benzoic acid in water, but less soluble in alcohol. It remains unaltered at the temperature at which benzoic acid melts and sublimes: at a higher temperature, it melts and gives off benzoic acid, the residue turning brown, and emitting the odour of burnt tartar. A cold saturated solution of the acid forms no precipitate with ferric chloride, lime-water, or silver-nitrate, but a slight precipitate with basic acetate of lead. When saturated with ammonia, it forms a pale-yellow precipitate with ferric chloride, none with chloride of calcium. In a solution of the acid one-fourth saturated with ammonia, nitrate of silver forms a white precipitate, consisting of *argentic benzotartrate*, $C^{11}H^8Ag^2O^7$.

Dibromotartaric Acid, $C^4H^4Br^2O^6$, is formed by the action of bromine, at 100°, on bromomaleic acid (iii. 788); probably thus:

$$C^4H^3BrO^4 + Br^4 + 2H^2O = 3HBr + C^4H^4Br^2O^6.$$

It is very deliquescent. (Kekulé, Jahresb. 1861, p. 363.)

Nitrotartaric Acid, $C^4H^4N^2O^{10} = \left.\begin{matrix}(NO^2)^2\\(C^4H^2O^2)^{iv}\\H^2\end{matrix}\right\}O^4$. (Dessaignes, Ann. Ch. Pharm. lxxxii. 362; lxxxix. 339.)—This acid is formed by adding 1 pt. of pulverised tartaric acid to 4½ pts. of very strong nitric acid; then adding, with stirring, an equal volume of strong sulphuric acid; pressing the pasty mass between porous tiles; dissolving it in a small quantity of lukewarm water; cooling to 0°, and pressing the crystals between paper.

Nitrotartaric acid dissolves in absolute alcohol, and remains, on spontaneous evaporation, in distinct prisms. It is optically active, like tartaric acid (Chautard). It is very unstable, its aqueous solution, even at a few degrees above 0°, continually giving off nitric oxide and carbonic anhydride. By spontaneous evaporation, it yields tartronic acid (p. 698), and, when heated to 40°—50°, oxalic acid.—By *sulphide of ammonium* it is reconverted into tartaric acid.

The nitrotartrates have not been much examined.—The *acid ammonium-salt*, $\left.\begin{matrix}H\\NH^4\end{matrix}\right\}C^4H^2(NO^2)^2O^6$, forms small, very soluble crystals.—The *neutral ammonium-salt* yields, with nitrate of silver, an easily soluble silver-salt, containing $Ag^2C^4H^2(NO^2)^2O^6$.

TARTARIC AMIDES. See TARTRAMIC ACID and TARTRAMIDE.

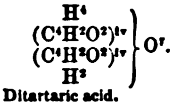
TARTARIC ANHYDRIDES. Since tartaric acid contains four atoms of replaceable hydrogen, it should be capable of yielding two anhydrides, by the loss of H^2O and $2H^2O$ respectively: thus—

$$\underset{\text{Tartaric acid.}}{\left.\begin{matrix}(C^4H^2O^2)^{iv}\\H^4\end{matrix}\right\}O^4.} \qquad \underset{\text{First anhydride.}}{\left.\begin{matrix}C^4H^2O^2)^{iv}\\H^2\end{matrix}\right\}O^3.} \qquad \underset{\text{True anhydride.}}{(C^4H^2O^2)^{iv}.O^2.}$$

But as the four typic hydrogen-atoms of tartaric acid are not all of the same character (two being alcoholic and two basic), it is further possible that the first anhydride may exhibit three isomeric modifications, according as the alcoholic or basic hydrogen-atoms of the acid are eliminated in its formation: thus—

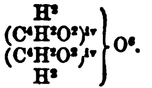
$$\underset{\text{Dibasic acid.}}{\left.\begin{matrix}(C^4H^2O^2)^{iv}\\H^2\end{matrix}\right\}O^3.} \qquad \underset{\text{Monobasic acid.}}{\left.\begin{matrix}H\\(C^4H^2O^2)^{iv}\\H\end{matrix}\right\}O^3.} \qquad \underset{\text{Neutral anhydride.}}{\left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\end{matrix}\right\}O^3.}$$

Further, two or more molecules of tartaric acid may unite together in giving up water, thereby producing compounds analogous to the polyethylenic alcohols (ii. 570), the polyglycerins (ii. 894), and the polylactic acids (iii. 461). The simplest, and therefore the most probable of these compounds, would be ditartaric acid, which, by further elimination of water, might yield corresponding anhydrides: thus—



$$\left.\begin{matrix}H^4\\(C^4H^2O^2)^{iv}\\(C^4H^2O^2)^{iv}\\H^2\end{matrix}\right\}O^7.$$

Ditartaric acid.



$$\left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\(C^4H^2O^2)^{iv}\\H^2\end{matrix}\right\}O^6.$$

Ditartaric anhydride.

All these compounds might possibly be produced by the action of heat upon tartaric acid. Only a few of them have, however, been actually obtained; and, moreover, the statements of different chemists, who have investigated the decompositions of tartaric acid by heat, do not quite agree. (See especially Braconnot, Ann. Ch. Pharm. ii. 315.—Frémy, *ibid.* xix. 197; xxix. 142; lxxviii. 297.—Erdmann, *ibid.* xxi. 9.—Laurent and Gerhardt, *ibid.* lxx. 348.) But, as already observed (p. 675), it appears most probable that the first effect of heat on tartaric acid is to convert it into the isomeric compound, metatartaric acid; and that afterwards, by successive elimination of water, there are formed—first, ditartaric acid, then a soluble modification of the first anhydride, $C^4H^4O^5$, called by Frémy tartrelic acid; and, finally, the neutral insoluble modification of the same anhydride. The true anhydride of tartaric acid, $C^4H^2O^2.O^2$, is not known. (Kekulé, *Lehrbruch*, ii. 199.)

Ditartaric Acid, $C^8H^{10}O^{11} = 2C^4H^6O^6 - H^2O$.—This acid (called *Tartralic acid* by Frémy, *Isotartaric acid* by Laurent and Gerhardt) is produced by melting tartaric acid, and keeping it at a temperature of 170°, till it no longer gives a precipitate of calcic tartrelate with lime, or with calcic acetate (Frémy); also by adding tartaric anhydride to melting tartaric acid (Schiff, Zeitschr. Ch. Pharm. 1862, p. 375). It is very soluble in water, and not crystallisable. Its salts, $C^8H^9M'O^{11}$ and $C^8H^8M''O^{11}$, even the calcium-salt, are also very soluble in water, and are precipitated by alcohol in the form of syrup or of bulky flocks. By boiling with water, they are converted, first into acid metatartrates, and then into tartrates.

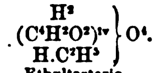
Gerhardt (*Traité*, ii. 15, 51) regards tartralic acid as isomeric with tartaric and metatartaric acids, on the ground that tartaric acid may be converted into it without loss of weight, even in presence of water. According to this view, the composition of the tartralates, which are neutral, is the same as that of the acid tartrates and metatartrates; but analysis shows that the composition of these salts agrees more nearly with the formula of the ditartrates above given.

Tartrelic Acid, $C^4H^4O^5 = C^4H^6O^6 - H^2O$. *Soluble Tartaric Anhydride.*—Obtained by quickly heating small quantities of tartaric acid till the fused mass swells up. It is a yellowish, tumefied, deliquescent mass, which dissolves in water, forming an acid solution.

Chloride or acetate of calcium added to this solution, throws down *tartrelate of calcium*, $C^8H^6Ca''O^{10}$, as a syrupy mass, which is insoluble in water, and becomes crystalline by contact with alcohol. The *barium-* and *strontium-salts*, which are similar in composition, and prepared in like manner, are also syrupy masses, insoluble in water. Tartrelic acid, heated with lead-oxide to 150°, yields a *lead-salt* containing $C^4H^4Pb''O^5$.—In contact with *alkalis*, it forms tartralates or ditartrates. By boiling with water, it is converted, first into metatartaric, then into tartaric acid.

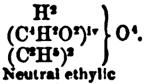
Insoluble Tartaric Anhydride, $C^4H^4O^5$, is formed by heating tartaric acid for some time to 150°, exhausting the product with cold water, and drying it in a vacuum. It is a white powder, insoluble in water, alcohol, and ether; and is converted by water, slowly in the cold, quickly on boiling, into tartaric acid. (Frémy.)

TARTARIC ETHERS. Tartaric acid, like other dibasic acids, forms, with monatomic acids, both acid and neutral ethers, the former of which are monobasic acids; *e.g.*:



$$\left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\H.C^2H^5\end{matrix}\right\}O^4.$$

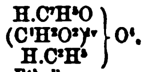
Ethyltartaric acid.



$$\left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\(C^2H^5)^2\end{matrix}\right\}O^4.$$

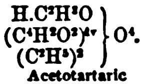
Neutral ethylic tartrate.

The two alcoholic hydrogen-atoms in these ethers are also replaceable by acid-radicles, forming compounds like the following:



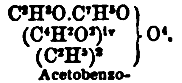
$$\left.\begin{matrix}H.C^7H^5O\\(C^4H^2O^2)^{iv}\\H.C^2H^5\end{matrix}\right\}O^4.$$

Ethylbenzotartaric acid.



$$\left.\begin{matrix}H.C^2H^3O\\(C^4H^2O^2)^{iv}\\(C^2H^5)^2\end{matrix}\right\}O^4.$$

Acetotartaric ether.



$$\left.\begin{matrix}C^2H^3O.C^7H^5O\\(C^4H^2O^2)^{iv}\\(C^2H^5)^2\end{matrix}\right\}O^4.$$

Acetobenzotartaric ether.

Closely related to these ethers are also certain dibasic acids, derived from tartaric acid by the substitution of acid-radicles for one or both of its alcoholic hydrogen-atoms (p. 689); *e.g.*:

$$\left.\begin{matrix} H.C^7H^5O \\ (C^4H^2O^2)^{iv} \\ H^2 \end{matrix}\right\} O^4. \qquad \left.\begin{matrix} (C^2H^3O)^2 \\ (C^4H^2O^2)^{iv} \\ H^2 \end{matrix}\right\} O^4. \qquad \left.\begin{matrix} (NO^2)^2 \\ (C^4H^2O^2)^{iv} \\ H^2 \end{matrix}\right\} O^4.$$

Benzotartaric acid. Diacetotartaric acid. Dinitrotartaric acid.

The constitution of these compounds shows that tartaric acid may be regarded as a diatomic alcohol, as well as a dibasic acid.

The acid tartaric ethers are formed by the direct action of tartaric acid on the alcohols; the neutral ethers by passing hydrochloric acid gas into a solution of the acid in the respective alcohols. The derivatives of these ethers containing acid radicles, are formed by treating them with alcoholic chlorides.

A few ethers are also known, produced by the action of tartaric acid on polyatomic alcohols.

Neutral Tartaric Ethers, containing Monatomic Alcohol-radicles.

Ethylic Tartrate, or **Tartaric Ether,** $C^8H^{14}O^6 = C^4H^4(C^2H^5)^2O^6$. (Demondesir, Ann. Ch. Pharm. lxxx 301.)—This ether is a liquid which acts on polarised light. It bears a somewhat high temperature without decomposition, but, when heated to a certain point, gives off considerable quantities of pyrotartaric acid. It mixes in all proportions with *water*, *alcohol*, and common *ether*.—With *ammonia* it yields tartramic acid or tartramide, according to the time for which the action is continued.

Tartaric ether is decomposed by *sodium*, with evolution of hydrogen; the action is slow, on account of the viscidity of the ether, but may be made to go on very rapidly, by mixing it with five or six times its volume of anhydrous benzene. On separating the excess of sodium, and evaporating, a pale yellowish-brown, uncrystalline, but friable residue, is obtained, probably consisting of sodiotartaric ether—$\left.\begin{matrix} H.Na \\ C^4H^2O^2 \\ (C^2H^5)^2 \end{matrix}\right\} O.$

By the continued action of the sodium, a gelatinous product is also formed, probably disodiotartaric ether, $\left.\begin{matrix} Na^2 \\ C^4H^2O^2 \\ (C^2H^5)^2 \end{matrix}\right\} O^4.$ (Perkin.)

Acetotartaric Ether, $C^{10}H^{16}O^7 = C^4H^3(C^2H^3O)(C^2H^5)^2O^6$. (Perkin, Chem. Soc. J. xx. 145.)—Produced by the action of acetylic chloride on an equivalent quantity of tartaric ether; the action takes place at ordinary temperatures, large quantities of hydrochloric acid being evolved, and the mixture becoming hot. The oily product is purified by agitating it with water, dissolving in ether, agitating the ethereal solution with dry carbonate of sodium, filtering, and evaporating to dryness over the water-bath.

Acetotartaric ether is an oily liquid, having about the consistence of olive-oil, heavier than water, and slightly soluble therein, but quite insoluble in saline solutions. It is perfectly neutral to test-paper, and has a rather bitter taste. When somewhat strongly heated in a retort, it decomposes, giving off acetic acid: at about 287°, an oil passes over, and finally a carbonaceous residue is left. It is decomposed by aqueous ammonia, the solution, when evaporated, yielding a yellowish syrupy product, having a bitter and slightly burning taste. Heated with *chloride of benzoyl*, it gives off hydrochloric acid, and forms a thick colourless oil, probably benzacetotartaric ether.

Acetotartaric ether is rapidly decomposed by *sodium*, especially when diluted with benzene, hydrogen-gas being evolved, and a transparent gummy substance formed, probably consisting of sodacetotartaric ether, $C^4H^2Na(C^2H^3O)(C^2H^5)^2O^6$.

Diacetotartaric Ether, $C^{12}H^{18}O^8 = C^4H^2(C^2H^3O)^2(C^2H^5)^2O^6$. (Perkin, Chem. Soc. J. xx. 147.)—Produced by treating 1 at. tartaric ether with 2 at. chloride of acetyl, and, after the reaction has abated, heating the product for a short time to 100° in a sealed tube. When purified like the preceding, it solidifies to a beautiful crystalline mass, which may be separated from a small quantity of oily acetotartaric ether by strong pressure between bibulous paper, and then crystallised from water.

Diacetotartaric ether dissolves in all proportions in *alcohol* and common *ether*, and is precipitated from its alcoholic solution by water. When it is boiled with water, a considerable quantity dissolves, and the solution, on cooling, deposits it in splendid prismatic crystals more than 1½ inch long. It is slightly soluble in cold water, but on the addition of a strong solution of chloride of sodium, the liquid becomes cloudy, and the diacetotartaric ether crystallises out on standing.

Diacetotartaric ether melts to a colourless oil at 67°, and does not resolidify on cooling; but as soon as a small particle of the solid product is thrown into it, it begins to crystallise in tufts of needles, and in a few moments becomes perfectly solid. During crystallisation, it evolves heat sufficient to become quite hot to the hand. When strongly heated, it distils with only slight decomposition. It boils between 294° and 298°.

Diacetotartaric ether is not quickly decomposed by *aqueous potash*, or by cold *alcoholic ammonia.* It is scarcely acted upon by *sodium*, either in the fused state, or when dissolved in benzene.

Paratartaric (*racemic*) *ether* treated with chloride of acetyl yields acetoparatartaric and diacetoparatartaric ether, isomeric with the tartaric ethers just described. Monacetoparatartaric ether is a colourless oil. Diacetoparatartaric ether is a solid body, melting at 50·5°, boiling at about 298°, and distilling with slight decomposition. It dissolves in alcohol or ether in all proportions. It is deposited from its boiling aqueous solution, on cooling, in small tufts of needles, and, after long standing, sometimes forms short but very brilliant prisms on the sides of the vessel.

Benzotartaric Ether, $C^{15}H^{18}O^7 = C^4H^3(C^7H^5O)(C^2H^5)^2O^6$. (Perkin, Chem. Soc. J. xx. 139.)—Produced by heating chloride of benzoyl with a slight excess of tartaric ether to 100° for two or three hours. When purified, like the preceding compound, by agitation with carbonate of sodium, solution in ether, &c., it forms a viscid transparent oil, which, on standing (especially under water) for two or three weeks, is almost wholly converted into a mass of colourless prismatic crystals, which may be freed from oil by pressure.

Benzotartaric ether, when pure, is a white inodorous solid, heavier than water, and easily pulverised. It melts at 64°, and cools to a viscid oil, which does not solidify until it has stood for some considerable time; but the introduction of a minute piece of the solid product immediately causes it to commence crystallising; and this takes place with a very considerable elevation of temperature. It crystallises in transparent prisms. If strongly heated, it distils with decomposition. It is soluble in all proportions in *alcohol* and *ether*; slightly soluble in boiling *water*, the solution becoming milky and depositing oily drops on cooling; afterwards beautiful but small prismatic crystals separate. Its aqueous solution has a slightly bitter taste. Its solutions do not change the colour of litmus-paper.—Aqueous *potash* appears to be without action upon it. With *sodium* it liberates hydrogen, and appears to form a sodium-compound. When heated in a sealed tube to 100° with alcoholic *ammonia*, it slowly decomposes, and is apparently converted into benzoic acid, tartramide, benzotartramide, and alcohol.

Alcoholic potash quickly decomposes benzotartaric ether, yielding, if in excess, tartaric and benzoic acids; but if dilute solutions are used, and the quantity of potash present is not sufficient to produce complete decomposition, benzotartaric and ethylbenzotartaric acids are produced (p. 695). The formation of these products is represented by the following equations:

$$\underset{\text{Benzotartaric ether.}}{\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}C^4H^3(C^7H^5O)O^6} + H^2O = \underset{\text{Alcohol.}}{C^2H^6O} + \underset{\text{Ethylbenzotartaric acid.}}{\left.\begin{matrix}H\\C^2H^5\end{matrix}\right\}C^4H^3(C^7H^5O)O^6}.$$

$$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}C^4H^3(C^7H^5O)O^6 + 2H^2O = 2C^2H^6O + \underset{\text{Benzotartaric acid.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}C^4H^3(C^7H^5O)O^6}.$$

$$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}C^4H^3(C^7H^5O)O^6 + 3H^2O = 2C^2H^6O + \underset{\text{Tartaric acid.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}C^4H^4O^6} + \underset{\text{Benzoic acid.}}{C^7H^6O^2}.$$

Benzotartaric ether is not converted into dibenzotartaric ether by heating with chloride of benzoyl; neither does this compound appear to be produced by heating tartaric ether with 2 at. chloride of benzoyl.

Paratartaric ether heated with chloride of benzoyl, yields benzoparatartaric ether isomeric with benzotartaric ether, but melting at a much lower temperature, viz. 57°, and not crystallising so readily.

Acetobenzotartaric Ether, $C^{17}H^{20}O^8 = C^4H^2(C^2H^3O)(C^7H^5O)(C^2H^5)^2O^6$. (Perkin, Chem. Soc. J. xx. 145.)—Prepared by heating benzotartaric ether with a slight excess of chloride of acetyl to 140°—150°, in a sealed tube for three or four hours. It is a very thick colourless oil, heavier than water, showing no tendency to solidify, neutral to test-paper, very soluble in alcohol and ether.—Heated with *alcoholic potash*, it is completely resolved into alcohol, and acetic, benzoic, and tartaric acids:

$$C^{17}H^{20}O^8 + 4H^2O = 2C^2H^6O + C^2H^4O^2 + C^7H^6O^2 + C^4H^6O^6.$$

Succinotartaric Ether, $C^{20}H^{30}O^{14} = C^8H^6(C^4H^4O^2)''(C^2H^5)^4O^{12}$. (Perkin, Chem. Soc. J. xx. 143.)—This body, formed by the substitution of 1 at. succinyl for 2 at. hydrogen in a double molecule of tartaric ether, is prepared by heating 2 at. tartaric ether with 1 at. chloride of succinyl in a test-tube to 100°, as long as hydrochloric acid continues to go off:

$$2C^4H^4(C^2H^5)^2O^6 + (C^4H^4O^2)''Cl^2 = 2HCl + C^8H^6(C^4H^4O^2)''(C^2H^5)^4O^{12}.$$

The product, purified like the preceding, is an extremely thick oil, generally of a pale-yellow colour. It dissolves freely in *alcohol* and *ether*, forming neutral solutions. It is decomposed by alcoholic potash, and cannot be distilled without decomposition.

Methylic Tartrate, $C^6H^{10}O^6 = C^4H^4(CH^3)^2O^6$. *Methyltartaric Ether.*—Prepared like ethyltartaric ether, which it resembles. (Demondesir.)

β. *Acid Tartaric Ethers containing Monatomic Alcohol-radules.*

These are monobasic acids, produced by the direct action of alcohols on tartaric acid.

Amyltartaric Acid, $C^9H^{16}O^6 = C^4H^5(C^5H^{11})O^6$. *Tartramylic Acid.*—This acid, discovered by Balard (Ann. Ch. Phys. [3] xii. 309), and more fully investigated by Breunlin (Ann. Ch. Pharm. xci. 314), is prepared by digesting 150 pts. finely-pulverised tartaric acid, for several days (at about 130°), with 88 pts. rectified amylic alcohol. A syrupy liquid is then formed, which, by slow cooling, solidifies to warty masses of unctuous crystals, having an intensely bitter taste. They melt at a gentle heat, and dissolve in a small quantity of water, but a larger quantity of water separates the amyltartaric acid in oily drops. (Breunlin.)

The amyltartrates, $C^4H^4M(C^5H^{11})O^6$ and $C^8H^8M''(C^5H^{11})^2O^{12}$, are for the most part soluble in water. Most of them remain unaltered when their aqueous solutions are boiled, but they decompose when dried at 100°.

Amyltartrate of Barium, prepared by saturation, separates from its concentrated solution, in colourless, nacreous, crystalline laminæ, containing $C^8H^8Ba''(C^5H^{11})^2O^6.2H^2O$, which become dull when dried at a gentle heat, and are decomposed at 100°. They dissolve in alcohol, and, on adding water to the solution, the anhydrous salt, $C^8H^8Ba''(C^5H^{11})^2O^{12}$. is precipitated in white amorphous flakes.—The *calcium-salt*, $C^8H^8Ca''(C^5H^{11})^2O^{12}$, likewise obtained by neutralisation, remains, on evaporating its solution over oil of vitriol, as a friable saline mass, which dissolves very readily in water, and is not decomposed at 100°.—The *lead-salt*, obtained by precipitating the potassium-salt with acetate of lead, appears to be a basic salt.—The *potassium-salt*, obtained by decomposing the barium-salt with carbonate of potassium, separates, on evaporation and cooling, as a white crystalline mass, containing $C^4H^4K(C^5H^{11})O^6.H^2O$. It is sparingly soluble in cold, easily in boiling water, and gives off its water of crystallisation at 100°.—The *sodium-salt*, $C^2H^4Na(C^5H^{11})O^6$, prepared in like manner, separates, by evaporation over oil of vitriol, in soft, nodular, anhydrous crystals. The *silver-salt*, $C^4H^4Ag(C^5H^{11})O^6$, separates on cooling from a hot concentrated solution of the potassium-salt mixed with nitrate of silver, in tufts of needles having an adamantine lustre. (Breunlin.)

Ethyltartaric Acid, $C^6H^{10}O^6 = C^4H^5(C^2H^5)O^6$.—*Tartrethylic* or *Tartrovinic Acid.* (Marian, Trommsd. J. xiii. 2, 43.—Trommsdorff, *ibid.* xxiv. 1, 11.—Guérin-Varry, Ann. Ch. Phys. [2] lxii. 57.)—When absolute alcohol is boiled for some time with tartaric acid, and the liquid, after dilution with water, saturated with carbonate of barium, insoluble tartrate of barium is formed, together with a solution of the ethyltartrate, which is deposited in crystals on concentrating the liquid. This salt, decomposed with an equivalent quantity of sulphuric acid, yields ethyltartaric acid.

This acid crystallises in elongated prisms, with oblique bases; it is colourless, inodorous, tastes both sweet and sour, and quickly absorbs moisture from the air. It is very soluble in alcohol and in ether. Its aqueous solution is completely decomposed, by prolonged boiling, into alcohol and tartaric acid. It dissolves zinc and iron, with evolution of hydrogen.

Ethyltartaric acid is decomposed, by dry distillation, into alcohol, water, acetic ether, acetic acid, ethylene-gas, pyrotartaric acid, and other products.—*Nitric acid* converts it into acetic, carbonic, and oxalic acids.

The solution of ethyltartaric acid gives no precipitate with *potash* or *soda*, in whatever proportion the alkali may be added.—When added by drops to *baryta-water*, it forms a precipitate, which disappears, with the exception of a slight turbidity, as the liquid approaches neutrality, but reappears on adding an excess of the acid. These characters distinguish ethyltartaric acid from tartaric acid.—With *lime-water*, it forms a precipitate soluble in excess of the acid.

The ethyltartrates, $C^4H^4M(C^2H^5)O^6$ and $C^8H^8M''(C^2H^5)^2O^{12}$, usually crystallise well; they are unctuous to the touch, and without odour. Almost all of them are very soluble in water, less soluble in alcohol. On boiling their solutions, they are resolved into alcohol and tartrates.

The *ammonium-salt* is obtained, in silky fibres, by spontaneous evaporation of a solution of the acid saturated with carbonate of ammonium.—The *potassium-salt*, $C^4H^4K(C^2H^5)O^6$, forms colourless rhombic prisms, usually exhibiting the combination $\infty\breve{P}2 . \infty\breve{P}\infty . \breve{P}\infty . P$. Axes $a : b : c = 0{\cdot}2879 : 1 : 0.4174$. Angle $\infty\breve{P}2 : \infty\breve{P}2$ (brach.) $= 120° 8$; $\infty\breve{P}2 : \infty\breve{P}\infty = 101° 5'$; $\breve{P}\infty : \breve{P}\infty = 134° 41'$. Cleavage easy parallel to $\infty\breve{P}\infty$. Its aqueous solution, when boiled, deposits acid tartrate of potassium.—The *sodium-salt* forms laminæ, sometimes rhomboïdal, sometimes rectangular.

The *barium-salt*, $C^8H^8Ba''(C^2H^5)^2O^{12}.2H^2O$, prepared as already described (p. 694), forms beautiful fan-shaped groups of crystals, apparently belonging to the trimetric system.

The *calcium-salt*, $C^8H^8Ca''(C^2H^5)^2O^{12}.5H^2O$, prepared like the barium-salt, forms rectangular prisms or laminæ, which melt in their water of crystallisation at 100°.

The *cupric salt*, $C^8H^8Cu''(C^2H^5)^2O^{12}.6H^2O$, obtained by dissolving cupric oxide in the aqueous acid, forms blue, silky, efflorescent needles.

The *lead-salt* separates, on adding ethyltartaric acid to acetate of lead, in small nacreous prisms, insoluble in excess of the acid.

The *silver-salt*, $C^4H^4Ag(C^2H^5)O^6$, obtained by precipitation, crystallises in prisms, sometimes tumefied in the middle. It is slightly soluble in cold water, and may be heated to 100° without decomposition.

The *zinc-salt* forms groups of rectangular prisms, unctuous to the touch.

Ethylbenzotartaric Acid, $C^{13}H^{14}O^7 = C^4H^3(C^7H^5O)(C^2H^5)O^6$. (Perkin, Chem. Soc. J. **xx.** 142.)—Produced, together with benzotartaric acid and other products, by treating a dilute alcoholic solution of benzotartaric ether with a quantity of dilute alcoholic potash, not sufficient to resolve it completely into benzoic and tartaric acids (p. 693). On gently heating the resulting liquid to expel the excess of alcohol, adding water to separate oily products, passing the solution through a wet filter, acidulating with hydrochloric acid, which separates an oil consisting of benzoic and ethylbenzoic acids, together with a little neutral oil, smelling like benzoic ether, and placing the clear filtrate in a vacuum over oil of vitriol, ethylbenzoic acid separates, after a few days, in beautiful tufts of hard needles, which may be completely purified by washing with water. The mother-liquor contains benzotartaric acid (p. 690).

Ethylbenzotartaric acid is sparingly soluble in water, but extremely soluble in alcohol and ether, and is deposited from its alcoholic or ethereal solution, on evaporation, in fan-shaped groups of crystals. Its aqueous solution reddens litmus-paper. It is easily decomposed by potash, and its salts appear to be rather unstable.

Methyltartaric Acid, $C^5H^8O^6 = C^4H^5(CH^3)O^6$. *Tartromethylic Acid.* (Dumas and Péligot, Ann. Ch. Phys. [2] lxi. 200.—Guérin-Varry, *ibid.* lxii. 77.—Dumas and Piria, *ibid.* [3] v. 373.)—Tartaric acid dissolves in methylic more easily than in ethylic alcohol, and converts it with greater facility into the acid ether. To prepare this compound, tartaric acid is dissolved in an equal weight of methylic alcohol at the boiling heat; the solution is evaporated to a syrup at a temperature below 100°; the syrup left to evaporate freely, and the resulting crystals dried in a vacuum.

Methyltartaric acid crystallises in colourless rectangular prisms, heavier than water, fusible, inodorous, but having an acid taste. It is scarcely altered by the moisture of the air, dissolves very easily in cold water, and in all proportions of boiling water; is easily soluble also in alcohol and wood-spirit, but insoluble in ether.

The aqueous solution of methyltartaric acid, when boiled, takes up 1 at. water, reproducing tartaric acid and methylic alcohol. The crystals, when heated, give off water, methylic alcohol, and methylic acetate, together with other products.

The aqueous acid dissolves *zinc* and *iron*, with evolution of hydrogen. With *baryta-water* and *lime-water* it forms precipitates, soluble in a slight excess of the acid. It does not precipitate sulphate of potassium, but forms a pulverulent precipitate with *acetate of lead.*

The methyltartrates are converted, by boiling their aqueous solutions, into methylic alcohol.—The *potassium-salt*, $C^5H^7KO^6$, crystallises in right rectangular prisms, which (according to Dumas and Piria) are anhydrous, but (according to Guérin-Varry) give off 4·2 per cent. water in a vacuum over oil of vitriol. It is much more soluble in hot than in cold water.—The *sodium-salt* is sparingly soluble in water, and separates, as a granular precipitate, on pouring methyltartaric acid into caustic soda.—The *barium-salt*, $C^{10}H^{14}Ba''O^{12}.H^2O$ (?), is obtained by saturating a solution of the acid in methylic alcohol with carbonate of barium, and crystallises, by spontaneous evaporation, in white rectangular prisms, much more soluble in hot than in cold water. It decomposes at about 160°, yielding a syrupy alliaceous liquid, containing water, methylic alcohol, methylic acetate, and a crystallisable substance, which may be obtained from it by evaporation.—The *lead-salt* and the *silver-salt* are obtained by precipitation.

Acids isomeric with Methyltartaric Acid.

Citratartaric Acid, $C^5H^8O^6$. (Carius, Ann. Ch. Pharm. cxxix. 159; Jahresb. 1864, p. 393.)—An acid produced by boiling a neutral salt of chlorocitramalic acid with water:

$$\underset{\text{Chlorocitramalate.}}{C^5H^5K^2ClO^5} + H^2O = KCl + \underset{\text{Citratartrate.}}{C^5H^7KO^6}.$$

To prepare it, a solution of chlorocitramalate of barium * is repeatedly evaporated to dryness, with excess of baryta. On carefully decomposing the resulting barium-salt with dilute sulphuric acid, evaporating the filtrate, and decolorising with animal charcoal, citratartaric acid is obtained, as a transparent, amorphous, deliquescent mass, which melts above 100°, and becomes carbonised, with evolution of acid vapours.

Citratartaric acid is dibasic. Its *potassium-* and *ammonium-salts* have the composition $C^5H^6M^2O^6$: the former crystallises in needles. The free acid is precipitated by acetate of lead; the solutions of the neutral alkali-metal salts form, with lead- and silver-salts, precipitates which are soluble both in the free acid and in excess of the alkaline salt; no precipitate with chloride of barium, calcium, copper, or zinc. Citratartaric acid reduces an ammoniacal silver-solution at the boiling heat, and prevents the precipitation of ferric oxide by alkalis.

Citratartrate of barium contains $C^5H^6Ba''O^6$; the *neutral lead-salt*, $C^5H^6Pb''O^6$; the *basic lead-salt*, $C^5H^6Pb''O^6.Pb''O$.

Dibasic acids having the same composition, and perhaps identical with the preceding, are produced:—*α*. By the reduction of oxalic ether with sodium-amalgam, the pasty amalgam being covered with alcohol of 80 per cent., and the oxalic ether gradually added.† This acid, Löwig's glycomalic acid, is uncrystallisable, but its acid barium-salt may be obtained in crystals. (Löwig, Jahresb. 1862, p. 311.)

β. By the action of silver-oxide on dibromopyrotartaric acid (iv. 774):

$$C^5H^6Br^2O^4 + Ag^2O + H^2O = 2AgBr + C^5H^8O^6.$$

The acid thus produced (homotartaric acid) is very soluble in water, and the syrupy solution yields crystals after long standing. Its salts are almost all soluble in water.—The *neutral barium-salt*, $C^5H^6Ba''O^6$ (at 150°), is insoluble in alcohol. (Kekulé, Ann. Ch. Pharm. Suppl. i. 346; *Lehrbuch*, ii. 213.)

γ. Tartaric Ethers containing Polyatomic Alcohol-radicles.

These ethers are formed by heating tartaric acid, in various proportions, with glycerin, mannite, dulcite, pinite, glucose, &c. Their composition and properties have already been described. See Ethers (ii. 521, 522); Glucosotartaric Acid (ii. 872); Glycerotartaric Acids (ii. 893).

TARTARIN. Native sulphate of potassium, also called *Arkanite* and *Glaserite.*

TARTARUS. A general pharmaceutical name for salts of tartaric acid:—*Tartarus ammoniatus* is ammonio-potassic tartrate.—*T. boraxatus*, or tartarised borax, is the gummy salt obtained by evaporating a mixture of 1 pt. borax and 3 pts. cream of tartar (p. 687).—*T. chalybeatus* is potassio-ferric tartrate.—*T. emeticus*: potassio-antimonious tartrate.—*T.* (*ferratus* or *ferruginosus*), *T. kalico-ferricus*, and *T. martialis* or *martiatus*, are various preparations containing ferric tartrate.—*T. regeneratus*: acetate of potassium.—*T. solubilis*: neutral tartrate of potassium.—*T. solubilis ammoniacalis*: ammonio-potassic tartrate.—*T. stibiatus*: tartar-emetic.—*T. tartarisatus*: neutral tartrate of potassium.—*T. vitriolatus*: sulphate of potassium.—*T. vitriolatus acidus*: acid sulphate of potassium.

TARTRALIC ACID. Syn. with Ditartaric Acid (p. 691).

TARTRAMETHANE. Ethylic tartramate.

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* This salt is prepared by treating a cold solution of citraconate of barium with hypochlorous acid, produced by passing chlorine into water containing mercurous oxide in suspension. (Jahresb. 1863, p. 386.)

† The reduction of ethylic oxalate by sodium-amalgam, under different conditions, yields racemocarbonic or desoxalic acid, $C^5H^6O^8$ (p. 40).

TARTRAMIC ACID. $C^4H^7NO^5 = C^4H^5(NH^2)O^5 = \left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\H.H^2\end{matrix}\right\}\begin{matrix}O^3\\N\end{matrix}$. (Laurent, Compt. Chim. 1845, p. 153.—K. Grote, Ann. Ch. Pharm. cxxx. 262.)—The ammonium-salt of this acid is produced:—1. By passing ammonium-gas over tartaric anhydride moistened with alcohol. Two layers of liquid are then formed, the upper consisting of alcohol, and the lower of tartramate of ammonium (Laurent).—2. Together with tartaric acid, by heating tartaric ether with strong aqueous ammonia to 100°. The resulting solution first deposits efflorescent crystals of tartrate of ammonium, then hard crusts of the tartramate. The longer the action is continued, the greater is the quantity of tartrate produced, and in about a week the whole of the tartramate is converted into tartrate. (Grote.)

Tartramate of calcium is precipitated on mixing the solution of the ammonium-salt with chloride of calcium, and adding alcohol. It is very soluble in water, insoluble in alcohol, and forms large tetrahedral crystals, containing $C^8H^{12}Ca''N^2O^{10}.6H^2O$. Its solution, mixed with acetate of lead and ammonia, yields a precipitate, consisting of a *basic lead-salt*, $C^8H^8\overset{''}{Pb}{}^3N^2O^{10}$—The *barium-salt*, $C^8H^{12}Ba''N^2O^{10}.8H^2O$, forms crystalline crusts, which give off half their water at 100.°—The *free acid*, separated from the calcium-salt by sulphuric acid, is syrupy. (Grote.)

Ethylic Tartramate, Tartramic Ether, or *Tartramethane*, is obtained by the action of alcoholic ammonia on tartaric ether. When cautiously treated with alkalis, it yields tartramic acid. Ammonia converts it into tartramide. (Demondesir, Compt. rend. xxxiii. 229.)

PHENYLTARTRAMIC, or TARTRANILIC ACID, $C^{10}H^{11}NO^5 = C^4H^6(C^6H^5)NO^5$. (Arppe, Ann. Ch. Pharm. xciii. 352; Jahresb. 1855, p. 477.)—This compound is obtained by boiling tartranil with aqueous ammonia. On evaporating the excess of ammonia at a gentle heat, adding an excess of baryta-water, decomposing the washed precipitate with sulphuric acid, and filtering, the tartranilic acid separates in light red warty masses and shining laminæ, which may be rendered colourless by treatment with animal charcoal.

Tartranilic acid is very soluble in *water* and in *alcohol*, less soluble in *ether*; it melts at 180°, and decomposes with loss of water.—Its *ammonium-salt* remains, on evaporation, as a very efflorescent, easily soluble, crystalline mass. The aqueous acid is not precipitated by *lime-water*, even on addition of ammonia; but on addition of potash, a cloudiness is produced, and a precipitate on boiling; neither is the aqueous acid precipitated by *chloride of barium* or *calcium*, even on addition of ammonia; with *baryta-water* it forms a copious precipitate, and with *ferric chloride*, a yellow precipitate.

Tartranilate of Barium, $C^{20}H^{20}Ba''N^2O^{10}$, is moderately soluble in boiling water, and crystallises in shining spangles.—The *silver-salt*, $C^{10}H^{10}AgNO^5$, is a white somewhat soluble powder.

TARTRAMIDE. $C^4H^8N^2O^4 = C^4H^4(NH^2)^2O^4 = \left.\begin{matrix}H^2\\(C^4H^2O^2)^{iv}\\H^4\end{matrix}\right\}\begin{matrix}O^2\\N^2\end{matrix}$. (Demondesir, *loc. cit.*—Pasteur, Compt. rend. xxxv. 176.—Grote, *loc. cit.*)—Produced by passing dry ammonia-gas into an alcoholic solution of tartaric ether. It usually crystallises from pure water in holohedral crystals; but if a few drops of ammonia are added to the hot solution, the crystals deposited on cooling exhibit hemihedral faces, often very fully developed. Its solution exhibits dextro- or lævo-rotation, according to the kind of tartaric acid from which it has been prepared. Both varieties unite with ordinary active *malamide*, forming compounds which have the same composition, but differ in crystalline form and in solubility, the compound containing lævotartramide being much more soluble than the other. (Pasteur.)

A hot solution of *mercuric oxide* in tartramide deposits crystalline crusts of mercurotartramide, $C^{16}H^{16}\overset{''}{Hg}{}^3N^8O^{16}$ (?), insoluble in water, soluble in hydrochloric acid, not attacked by iodide of ethyl. (Grote.)

Oxide of silver is easily reduced by tartramide. (Grote.)

DIPHENYLTARTRAMIDE, or TARTRANILIDE, $C^{16}H^{16}N^2O^4 = C^4H^6(C^6H^5)^2N^2O^4$. (Arppe, Ann. Ch. Pharm. xciii. 352.)—Produced, together with tartranil (phenyltartrimide), by the action of heat on tartrate of aniline. This salt, heated to 130°—140°, gives off aniline (the neutral salt being partly converted into the acid salt); and at 150°, the mass fuses, and then no longer gives the reaction of aniline with chloride of lime:

$$\underset{\text{Neutral tartrate of aniline.}}{C^4H^4(C^6H^8N)^2O^6} - 2H^2O = \underset{\text{Tartranilide.}}{C^{16}H^{16}N^2O^4}.$$

$$\underset{\text{Acid tartrate of aniline.}}{C^4H^5(C^6H^8N)O^6} - 2H^2O = \underset{\text{Tartranil.}}{C^{10}H^9NO^4}.$$

Boiling water dissolves out the tartranil; the brown residue dissolves in boiling alcohol; and the solution, on cooling, deposits crystals of tartranilide.

Tartranilide crystallises in colourless, nacreous, slender, interlaced needles, insoluble in water, slightly soluble in ether, moderately soluble in alcohol. It may be heated to 250° without decomposition, melts and decomposes at a higher temperature, but by careful heating to somewhat below its melting-point, it may be sublimed in shining laminæ. It is not altered by boiling with alkaline solutions. It is dissolved with difficulty by hot hydrochloric acid, with partial decomposition by nitric acid, easily by sulphuric acid.

TARTRAMYLIC ACID. Syn. with Amyltartaric Acid (p. 694).

TARTRANIL. Syn. with Phenyltartrimide (*infra*).

TARTRANILIC ACID. Syn with Phenyltartramic Acid (p. 697).

TARTRANILIDE. Syn. with Phenyltartramide (p. 697).

TARTRATES. See Tartaric Acid (p. 675).

TARTRELIC ACID. Soluble tartaric anhydride (p. 691).

TARTRETHYLIC ACID. Syn. with Ethyltartaric Acid (p. 694).

TARTRIMIDE. $C^4H^5NO^4 = \left.\begin{matrix}H^2\\(C^4H^2O^2)''\\H\end{matrix}\right\}\begin{matrix}O^2\\N\end{matrix} = C^4H^4(NH^4)O^6$ (acid ammonium-tartrate) $-2H^2O$.—This compound has not been obtained; but phenyltartrimide or tartranil, $C^{10}H^9NO^4 = C^4H^4(C^6H^5)NO^4$, is produced, as above described, together with tartranilide, by the dehydration of tartrate of aniline. It may be purified by recrystallisation and treatment with animal charcoal, and separates, on cooling from hot solutions, as a white granular powder, or in nacreous laminæ. It dissolves easily in water and in alcohol, sparingly in ether. It may be heated to somewhat above 200° without decomposition (the granular variety becoming crystalline, and partly volatilising as a woolly sublimate), but melts, and decomposes at 230°. It is tasteless, but reddens litmus-paper distinctly. (Arppe, *loc. cit.*)

TARTROGLYCERIC ACID. Syn. with Glycerotartaric Acid (ii. 893).

TARTROMETHYLIC ACID. Syn. with Methyltartaric Acid (p. 695).

TARTRONIC ACID. $C^3H^4O^5$. (Dessaignes, Compt. rend. xxxiv. 731; xxxviii. 44.)—A dibasic acid, produced by the spontaneous decomposition of nitrotartaric acid (p. 690); also, according to Baeyer (Jahresb. 1864, p. 641), by the action of sodium-amalgam on mesoxalic acid, $C^3H^2O^5$ (iii. 932). It crystallises in rather large prisms, which melt at 160°, and decompose with formation of glycollide (ii. 919):

$$C^3H^4O^5 = C^2H^2O^2 + CO^2 + H^2O.$$

The tartronates of the alkali-metals are soluble in water: the *acid ammonium-salt* crystallises in prisms: the *silver-salt* contains $C^3H^2Ag^2O^5$.—The aqueous acid forms precipitates with argentic, plumbic, and mercurous salts, and with the acetates of barium, calcium, and copper.

TARTROVINIC ACID. Syn. with Ethyltartaric Acid (p. 694).

TARTRYL. $C^4H^2O^2$.—The radicle of tartaric acid.

TARTRYLIC ACID. Syn. with Tartaric Acid.

TASMANITE. A fossil resin occurring, in small scales or plates, between the layers of a rock containing alumina and ferric oxide, occurring on the Mersey River in Tasmania. The resin, which forms from 30 to 40 per cent. of the entire deposit, is translucent and reddish-brown, has a specific gravity of 1·18, hardness = 2, and a conchoïdal fracture. It is not dissolved by alkalis, alcohol, ether, carbonic disulphide, benzene, or other hydrocarbons. It is slowly oxidised by nitric acid, with formation of sulphuric acid; oil of vitriol chars it, and eliminates sulphydric acid. By dry distillation, it yields oily and solid products, smelling like Canadian petroleum. It burns readily in the air, with a smoky flame and offensive odour. It gives by analysis (after deduction of 8 to 12 per cent. ash, consisting of silica, alumina, and a little ferric oxide), 79·34 per cent. carbon, 10·41 hydrogen, 5·32 sulphur, and 4·94 oxygen, agreeing nearly with the formula $C^{40}H^{62}O^2S$. (Church, Phil. Mag. [4] xxviii. 465.)

TAUNUS-SLATE. A clay-slate occurring in the Taunus range in Western Germany. It has a grey to violet colour, and silky iridescent lustre, and contains sericite or damourite (p. 235). A similar formation occurs at Göllnitz in Hungary.

TAURINE. $C^2H^7NSO^3$.—A neutral crystallisable substance obtained from bile, and resulting from the transformation of taurocholic acid under the influence of acids or of alkalis:

$$\underset{\substack{\text{Taurocholic}\\\text{acid.}}}{C^{26}H^{45}NSO^7} + H^2O = \underset{\text{Taurine.}}{C^2H^7NSO^3} + \underset{\substack{\text{Cholic}\\\text{acid.}}}{C^{24}H^{40}O^5}.$$

It was discovered in 1826 by L. Gmelin (Tiedemann u. Gmelin, *Die Verdauung*, i. 43, 60), who obtained it from ox-bile; it may also be prepared from the bile of most other animals—from all kinds of bile, indeed, which contain taurocholic acid (Strecker, Ann. Ch. Pharm. lxv. 132; lxvii. 34; xci. 101).—It is never found in the free state in healthy bile, or indeed in any other of the healthy secretions, at least in the higher animals; but it often occurs in diseased bile taken from the dead body, especially when the bile has an acid reaction. It is found also in certain molluscs (Valenciennes and Frémy, Compt. rend. xli. 735); in the muscles of the oyster, which close the shell; in the blood of the shark; in the liver, spleen, and kidneys of the ray (Städeler and Frerichs); in the pulmonary tissue of oxen, and sometimes in the kidneys (Clöetta, Ann. Ch. Pharm. xcix. 289). It has been especially studied by Demarçay (Ann. Ch. Pharm. xxvii. 286), by Dumas and Pelouze (*ibid.* xxvii. 292), and by Redtenbacher (*ibid.* lvii. 170), who first showed that it contains sulphur.

According to the formula above given, which was established by Redtenbacher, taurine is isomeric with acid sulphite of vinyl-ammonium, $\left.\begin{matrix}NH^3(C^2H^3)\\H\end{matrix}\right\}SO^3$, and is related to isethionic acid in the same manner as alanine to lactic acid:

$$\underset{\substack{\text{Lactate of}\\\text{ammonium.}}}{C^3H^5(NH^4)O^3} - H^2O = \underset{\text{Alanine.}}{C^3H^7NO^2}.$$

$$\underset{\substack{\text{Isethionate of}\\\text{ammonium.}}}{C^2H^5(NH^4)SO^4} - H^2O = \underset{\text{Taurine.}}{C^2H^7NSO^3}.$$

In accordance with this last relation, Strecker has shown that it may be produced from isethionate of ammonium by elimination of water, and an improved method of preparing it from isethionic acid has recently been given by Kolbe. (Ann. Ch. Pharm. cxxii. 33.)

Preparation.—1. From *Bile.*—Ox-bile (which is the kind most easily obtained in quantity) is mixed with hydrochloric acid, and the liquid filtered from the resulting precipitate is evaporated down at the boiling heat, till it has separated into a viscous resinous deposit and a clear watery liquid. The latter is poured off, the resin rinsed with water, and the united liquids concentrated. On cooling, they deposit a large quantity of common salt, together with crystals of taurine, which must be picked out and purified by recrystallisation.

Taurine is also easily prepared from putrid bile. The bile, mixed with a considerable quantity of water, is exposed for about three weeks to a summer temperature, till it acquires a distinct acid reaction. It is then precipitated with acetic acid; the filtered liquid is evaporated; the residue treated with strong alcohol; and the taurine, which remains undissolved, is crystallised from boiling water (Gorup-Besanez, Ann. Ch. Pharm. lix. 130). As taurine may be decomposed by prolonged contact with ferments, it is important not to allow the putrefaction to go on too long.

2. From *Isethionic Acid.*—*a.* Isethionate of ammonium is heated for some time to 210°, till it becomes solid; the residue is dissolved in water; and the solution mixed with a small quantity of alcohol, which throws down a brownish substance; then with a larger quantity, which precipitates taurine (Strecker). The product thus obtained is generally small, the greater part of the taurine suffering further decomposition.

β. Dry pulverised isethionate of potassium is mixed in a retort with 2½ times its weight of phosphoric pentachloride. The mixture immediately becomes warm, and gives off hydrochloric acid and phosphoric oxychloride, after which, on applying heat, chlorethylsulphuric chloride, $C^2H^4SO^2Cl^2$, distils over, together with more oxychloride. These two substances are separated by fractional distillation, and the chlorethylsulphuric chloride, which passes over at about 200°, is decomposed by prolonged heating with water in sealed tubes, into hydrochloric and chlorethylsulphuric acids. The resulting solution is neutralised with ammonia, and the salt left on evaporating it over the water-bath, is heated for some time to 100° in closed vessels with excess of strong aqueous ammonia, whereby taurine is produced, together with sal-ammoniac. The free ammonia is then evaporated off; the liquid heated with hydrate of lead as long as ammonia continues to escape; and the filtrate, freed from lead by sulphuretted hydrogen, is concentrated by evaporation: it then, on cooling, yields crystals of pure taurine (**Kolbe**). The series of reactions is represented by the following equations:—

$$\underset{\text{Isethionic acid.}}{C^2H^6SO^4} + 2PCl^5 = \underset{\text{Chlorethyl-sulphuric chloride.}}{C^2H^4SO^2Cl^2} + 2POCl^3 + 2HCl.$$

$$\underset{\text{Chlorethyl-sulphuric chloride.}}{C^2H^4SO^2Cl^2} + H^2O = HCl + \underset{\text{Chlorethyl-sulphuric acid.}}{C^2H^5ClSO^3}.$$

$$\underset{\text{Chlorethyl-sulphuric acid.}}{C^2H^5ClSO^3} + NH^3 = HCl + \underset{\text{Taurine.}}{C^2H^7NSO^3}.$$

Properties.—Taurine forms large, transparent, monoclinic crystals, having a vitreous lustre, and usually exhibiting the combination $\infty P \,.\, \infty P \infty \,.\, +P \,.\, -P$, like *fig.* 301 (ii. 155), also with oP and other faces. Axes $a : b : c = 1{\cdot}4648 : 1 : 0{\cdot}06648$. Angle $b : c = 86° 22'$; $\infty P : \infty P$ (orthod.) $= 68° 32'$; $oP : \infty P = 87°$; $+P : +P$ (clinod.) $= 137° 30'$; $-P : -P$ (clinod.) $= 139° 44'$. The crystals grate between the teeth, and have a pungent taste; they are neutral to vegetable colours, and permanent at 100°, but melt and carbonise at a higher temperature. By dry distillation, they yield a brown empyreumatic oil, together with a yellow slightly acid liquid, which contains an ammoniacal salt, and reddens ferric chloride (acetate of ammonium?).

Taurine is more soluble in hot than in cold water; 1 pt. dissolves in 15·5 pts. water at 12°. It is nearly insoluble in absolute alcohol.—Strong *sulphuric* and *nitric acids* dissolve it; but it is not decomposed by nitric or by nitromuriatic acid, even at the boiling heat, or by dry chlorine.—*Nitrous acid* converts it into isethionic acid, with evolution of nitrogen (**Gibbs**, Sill. Am. J. [2], xxv. 30). Its aqueous solution is not precipitated by salts of copper, mercury, or silver.—Melted with caustic *potash*, it yields a residue, which, when treated with dilute sulphuric acid, gives off sulphydric and sulphurous acids, and yields a deposit of sulphur. If evaporated slowly with caustic potash, it gives up all its ammonia at a certain stage, without blackening; and the cooled residue, if then treated with sulphuric acid, gives off sulphurous acid, without sulphydric acid or deposition of sulphur, and yields by distillation a mixture of acetic and sulphurous acids.

TAURISCITE. A variety of ferrous sulphate, found on the Windgälle, in the Canton Uri, Switzerland; it has the composition of ordinary green vitriol, but forms orthorhombic crystals, like those of magnesium-sulphate.

TAUROCHENOCHOLIC ACID. A sulphuretted acid contained in goose-bile. It has not been obtained quite pure, but, according to **Heintz** and **Wislicenus** (Pogg. Ann. cviii. 547), it consists of $C^{29}H^{49}NSO^3$, differing therefore in composition from taurocholic acid, and, when boiled with baryta-water, yields chenocholic acid, $C^{27}H^{44}O^4$, homologous with hyocholic acid, $C^{25}H^{40}O^4$. **Chenocholic acid** is insoluble in water, soluble in alcohol and ether, and separates from solution mostly as an amorphous mass, rarely in indistinct crystals. Its solution has an acid reaction, and gives, with sugar and sulphuric acid, the blood-red coloration characteristic of the biliary acids.—Its *barium-salt*, $C^{54}H^{86}Ba''O^8$, is insoluble in water and in ether, but soluble in absolute alcohol.—The *potassium-salt* dissolves easily in water and in alcohol, but not in dilute potash-ley.

TAUROCHOLIC ACID. $C^{26}H^{45}NSO^7$. *Choleic Acid. Sulphocholeic Acid.* (**Strecker**, Ann. Ch. Pharm. lxvii. 30; lxx. 169.—**Lieberkühn** and **Heintz**, *Lehrbuch der Zoochemie*, p. 367.—**Hoppe**, Arch. Path. Anat. xv. 126.—**Cloëtta** and **Vulpian**, N. Jahrb. Pharm. vii. 106.—**J. Parke**, Bull. Soc. Chim. 1866, ii. 242.)—An acid occurring as a sodium-salt in the bile of most animals. In the bile of serpents (*Boa*, *Python*), and in that of the dog, it occurs free from glycocholic acid; in that of fishes (*Pleuronectes*, *Gadus*, *Esox*, *Perca*), and of the sheep, wolf, goat, and domestic fowl, mixed with only a small quantity, and in that of the ox, with a large quantity of glycocholic acid.

Taurocholic acid may be prepared from dog's bile, by evaporating the decolorised alcoholic extract of the bile; digesting the residue with a small quantity of absolute alcohol, and adding ether, which precipitates the alkaline taurocholate in the crystalline state; mixing the aqueous solution of this salt with acetate of lead and a little ammonia; exhausting the washed precipitate with boiling alcohol; and saturating the hot filtered liquid with sulphydric acid gas. On evaporating the filtered liquid to a small bulk, and precipitating with excess of ether, the syrupy precipitate solidifies, after some time, into a mass of fine silky needles of pure taurocholic acid, which in contact with the air quickly changes to an amorphous transparent mass (Parke). Taurocholic acid may be prepared from bile containing also glycocholic acid, by first precipitating the latter with basic acetate of lead, and throwing down the taurocholic acid from the filtrate by adding more basic acetate of lead and ammonia. (Heintz.)

Taurocholic acid is easily soluble in water and in alcohol, less soluble in ether; it has a sweetish taste, with somewhat bitter aftertaste. It acts upon polarised light, its specific rotatory power being +24·9° for red, and +25·3° for yellow light (Hoppe-Seyler). In the dry state, it may be heated considerably above 100° without decomposition (Parke); but when boiled with *water*, or with *alkalis*, it is resolved into taurine and cholic acid:

$$C^{26}H^{45}NSO^7 + H^2O = C^2H^7NSO^3 + C^{24}H^{40}O^5.$$

By boiling with *acids*, it is resolved into taurine and dyslysin, $C^{24}H^{36}O^3$, together with other products:

$$C^{26}H^{45}NSO^7 = C^2H^7NSO^3 + C^{24}H^{36}O^3 + H^2O.$$

Taurocholates.—Taurocholic acid is monobasic. The taurocholates of the alkali-metals are easily soluble in water and in alcohol, but insoluble in ether, which precipitates them from their alcoholic solutions as pasty masses changing into crystals on standing. The aqueous solutions of the alkaline taurocholates froth like soap-water, and deposit the dissolved salt on addition of caustic potash. They give no precipitate with acetic acid, dilute mineral acids, or neutral acetate of lead.—*Basic acetate of lead* throws down white flocks, soluble in boiling water, and in excess of the lead-solution; on adding a few drops of ammonia, a more abundant precipitate is formed.—*Ferric chloride* produces a precipitate easily soluble in excess. No turbidity is produced by nitrate of silver or by mercuric chloride.—*Mercurous nitrate* and *stannous chloride* throw down white flocks. The solutions give no precipitate with acetate of barium, strontium, calcium, magnesium, or copper.

Taurocholate of Barium is obtained, by dissolving taurocholic acid in baryta-water, evaporating, dissolving in alcohol, and precipitating with ether, as a resinous mass, which quickly solidifies in the crystalline form.

Taurocholate of Lead.—The precipitate formed by basic acetate of lead in the solution of an alkaline taurocholate contains 52 at. carbon to 2½ at. lead.

Taurocholate of Potassium, $C^{26}H^{44}KNSO^7$, is contained in fish-bile, together with glycocholate of sodium. To obtain it pure, the bile is first precipitated by neutral acetate of lead; then the filtrate by basic acetate of lead and ammonia; the precipitate is decomposed by carbonate of potassium; and the solution is mixed with strong potash-ley, which precipitates the taurocholate of potassium. For further purification, it is dissolved in absolute alcohol; carbonic acid gas is passed into the solution; the liquid is filtered from the carbonate of potassium which separates; and the taurocholate is precipitated by ether. It then separates in colourless needles, grouped like crystals of wavellite.

Taurocholate of Sodium, $C^{26}H^{44}NaNSO^7$, is one of the chief constituents of ox-bile. It resembless the potassium-salt.

TAURYLIC ACID. $C^7H^8O^7$. (Stadeler, Ann. Ch. Pharm. lxxvii. 17.)—A compound obtained, together with phenol, from cows', horses', and human urine. It appears to be isomeric with anisol, benzylic alcohol, and cresol—perhaps identical with the latter; but its composition is not precisely known, as it has never been completely separated fron phenol.

To extract it, cows' urine is boiled with lime, and the decanted liquid is evaporated to an eighth of its bulk; supersaturated when cold with hydrochloric acid; left to stand for twenty-four hours; and then distilled, after separation of the hippuric acid deposited from it. The distillate, which contains thick greenish oily drops having a disagreeable odour, is mixed with a weighed quantity of potassium-hydrate and rectified (whereupon it gives off, together with ammonia, a neutral nitrogenous oil heavier than water, and having the odour of rosemary); the residue is mixed with a quantity of sulphuric acid sufficient to neutralise ⅝ths of the potash, and distilled, as long as the distillate is precipitated by basic acetate of lead; this distillate, which smells of phenol, is repeatedly rectified over common salt, till only a small quantity of watery liquid remains mixed with it, then repeatedly agitated with carbonate of sodium (to remove damolic and damaluric acids, ii. 301), and exhausted with ether; the ethereal solution is evaporated, the residue distilled, first with strong potash-ley to volatilise neutral oil, and then with acid carbonate of potassium; and this last oily distillate is dried over chloride of calcium and rectified, oil containing water then passing over at 180°, pure oil between 185° and 195°, and brownish oil at 200°.

The liquid which passes over between 185° and 195°, is a mixture of taurylic and phenic acids. It is a colourless oil, which smells like castoreum, remains liquid at 18°, and makes a white spot upon the skin. With an equal volume of strong sulphuric acid, it solidifies to a dendritic mass, the mother-liqour of which contains phenylsulphuric acid. When boiled with nitric acid, it yields a nitro-acid.

TAUTOCLINE. Breithaupt's name for a ferruginous bitter spar, from Freiberg, containing, according to Ettling (Ann. Ch. Pharm. xcix. 204), 49·07 per cent. $CaCO^3$, 33·28 $MgCO^3$, 14·89 $FeCO^3$, and 2·09 MnO^3 (= 99·33).

TAUTOLITE. A mineral allied to bucklandite, but regarded by Breithaupt as a distinct species, occurring in the volcanic rocks at Lake Laach, near Andernach. It is opaque, black, with vitreous lustre, and crystallised like bucklandite: hardness = 6·5; specific gravity = 3·865. It appears to consist mainly of the silicates of ferrosum, magnesium, and aluminium.

TAXIN. A resinous substance obtained from the leaves of the yew-tree (*Taxus baccata*), by treatment with alcohol and tartaric acid, two pounds of the leaves yielding 3 grains of taxin. It is slightly soluble in water, dissolves easily in alcohol, ether, and dilute acids, and is precipitated from the acid solutions by alkalis in white bulky flocks. It is not precipitated by tannic acid or tincture of iodine. Strong sulphuric acid dissolves it, with purple-red colour. (Lucas, Arch. Pharm. [2], lxxxv. 145.)

TAYUYIN. An amorphous, purgative, bitter substance, contained in the root of *Trianosperma ficifolia*, Mart., a climbing cucurbitaceous plant, indigenous in Brazil. (Peckolt, Arch. Pharm. [2], cxiii. 104.)

TCHA-LAN. A blue powder, containing copper, used by the Chinese for producing blue colours on porcelain. (Ebelmen and Salvétat, Ann. Ch. Phys. [3], xxxv. 338.)

TCHINGUEL-SAKESEY. A kind of caoutchouc, less elastic than the ordinary kind. It is said to flow from incisions in the stem of a tree cultivated in Kurdistan, and to harden in the air (*Handw. d. Chem.* viii. 525).

TEA. *Thé. Thee. Folia theæ.*—The dried leaves of the tea-plant, *Thea sinensis*. This plant is indigenous and extensively cultivated in China, Japan, and the northern parts of the eastern peninsula of India, and has been introduced more or less successfully into British India on the southern declivities of the Himalayas, Java, the Kong Mountains in Western Africa, Brazil, Madeira, and other countries of warm and temperate climates; it appears, indeed, to be capable of flourishing in all latitudes between 0° and 40°. It was formerly supposed that there were two species of the tea-plant, *Thea viridis*, yielding green, and *Thea Bohea*, yielding black tea; but it appears, from the recent observations of Mr. Fortune,* that either green or black tea may be obtained at pleasure from the same plant.

Green tea is prepared from the young leaves, which, within an hour or two after they have been gathered, are roasted in pans over a brisk wood-fire. After four or five minutes' roasting, the leaves become flaccid, and are rolled by the hands upon a wooden table; they are then again thrown into the drying-pans, where they are kept in rapid motion, and in about an hour, or an hour and a half, are completely dried.

Black tea is allowed to lie in heaps for ten or twelve hours after the leaves have been gathered; they are then tossed about for some time, till they become flaccid. At this stage they begin to emit a fragrant smell; they are next rolled in balls, with the hand, upon a wooden table, and a large quantity of liquid is expressed from them; after which they are shaken out, roasted for a few minutes, agained rolled, and, whilst still flaccid, are exposed to the air for some hours upon shallow bamboo trays: this alternate heating and rolling is repeated three or four times, and finally, the leaves are dried slowly over charcoal fires. A species of fermentation appears to occur during the drying of the leaf, in consequence of which a development of essential oil takes place, by which the agreeable aroma is occasioned: this aroma is wanting in the fresh leaf. The change of the leaf from green to black is mainly due to chemical alterations produced by the oxygen of the air upon the constituents of the leaf, and especially upon the astringent principle—this change being prevented in green tea by the rapid process of drying to which it is subjected.

Many kinds of green tea, intended for the European market, are coloured by dusting them with a finely-pulverised mixture of prussian-blue and gypsum, turmeric being also sometimes added; but the Chinese never colour tea intended for their own use. Teas for the foreign market are also frequently perfumed with various sweet-scented flowers—as roses, jasmine, orange, *Gardenia florida*, *Olea fragrans*, &c.

Tea is subjected to numerous adulterations. It is often mixed with various leaves

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* "The Tea Districts of China and India," by R. Fortune (3rd edition, London, John Murray, 1857), i. 220; ii. 237.

(as those of the elm, willow, sloe, &c.), dried and prepared like true tea-leaves; or it is mixed, during the colouring process above mentioned, with graphite, talc, &c. In some instances, preparations of copper have actually been used to give a green colour to tea (**Günther**, J. pr. Chem. x. 279.—**Warington**, Chem. Gaz. 1852, p. 238).—A kind of adulteration, which has been much practised in this country, is the working up of spent tea-leaves, which are prepared in the Chinese fashion, so as to resemble black and green tea. Sometimes also products are sent into the market as tea, or mixed in considerable quantities with various kinds of tea, which do not consist of tea-leaves at all, but are artificial mixtures, made out of tea-dust, sand, and dirt of various kinds, united together with paste. A substance of this kind is prepared in China, and called by the Chinese "Lie-tea," by the English "gum and dust."

Chemical Constitution of Tea.—The most important constituents of tea are, an *essential oil*, to which it owes its peculiar aroma; two nitrogenised bodies, viz., *theine* or *caffeine*, and *legumin*; and a peculiar astringent substance, or *tannin*.

Mulder (Ann. Ch. Pharm. xxviii. 314) analysed four kinds of tea, from China and Java. He found the proportion of water in all of them nearly the same, whereas **Péligot** (*ibid.* xlvii. 358) found the average amount of water equal to 10 per cent. in green tea, and 8 per cent. in black:—

Composition of Dried Tea. (**Mulder**.)

	Chinese Tea.		Java Tea.	
	Green (Hyson).	Black (Congo).	Green (Hyson).	Black (Congo).
Volatile oil . . .	0·79	0.60	0·98	0·65
Chlorophyll . . .	2·22	1·84	3·24	1·28
Wax	0·28	. .	0·32	
Resin	2·22	3·64	1·64	2·44
Gum	8·56	7·28	12·20	11·08
Tannin . . .	17·80	12·88	17·56	14·80
Theine . . .	0·43	0·46	0·60	0·65
Extractive matter . .	22·80	19·88	21·68	18·64
Extractive deposit* .	. .	1·48	. .	1·64
Extracted by hydrochloric acid	23·60	19·12	20·36	18·24
Albumin (? legumin) .	3·00	2·80	3·64	1·28
Woody fibre . . .	17·08	28·82	18·20	27·00
Ash	5·56	5·24	4·76	5·36
	104·34	104·04	105·18	103·06

The **volatile oil of tea** is obtained either by distillation, or by extraction with ether. It is lemon-yellow, lighter than water, easily solidifies, resinises quickly on exposure to the air, and possesses in a high degree the smell and taste of tea. It has a powerful stimulating action, and in rather large quantities produces giddiness and headache: in combination with tannin, however, it produces (according to **Mulder**) merely a diuretic and sudorific action.

The properties of **theine**, and the methods of extracting it from tea, have already been described under CAFFEINE (i. 707). The following are the proportions of it in various kinds of tea, as determined by **Stenhouse** (Ann. Ch. Pharm. xlv. 366; xlvi. 227; lxxxix. 245; cii. 126):—

Green Hyson tea	contains	1·05 per cent. theine.
Black Congo	„	1·02 „
„ Assam	„	1·37 „
Cheap green Twankay	„	0·98 „
Cheap black Bohea	„	0·70 „
Black tea (average) †	„	2·00 „
The same	„	2·13 „
Black Kumaon tea (Himalayas)	„	1·9 „

Péligot (Ann. Ch. Pharm xlvii. 361) found in Hyson tea 2·40 and 2·56 per cent. theine; in a mixture of equal parts of *Gunpowder*, *Hyson*, *Caper*, and *Kaisow tea*, 2·70; in *Gunpowder tea*, 3·5 and 4·1 per cent., and by a more complete method of extraction 6·21 per cent., of which 3·84 crystallised out from the concentrated solution, and 2·37 were obtained from the mother-liquor by precipitation with tannic acid.

The proportion of **nitrogen** in tea, dried at 100°, is (according to **Péligot**) in Pekoe tea 6·58, Gunpowder 6·15, Souchong 6·15, and Assam 6·10 per cent. The aqueous extract of 100 pts. dried Gunpowder tea yielded 4·30; of green Souchong, 4·70 per cent. nitrogen. The leaves, exhausted by hot water, contained, when dried, 4·6 per cent. (*Souchong*) and 4.40 per cent. (*Gunpowder*) nitrogen. The exhausted leaves contain casein (legumin), combined with tannin in the form of a compound insoluble in water, which may, however, be rendered soluble by addition of alkali. According to Péligot's determinations—

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* Oxidised extractive matter, according to **Warington** (Ann. Ch. Pharm. lxxxi. 233).

† **Gram, Stenhouse**, and **Campbell** (Chem. Soc. Qu. J. ix. 33).

100 pts. of Gunpowder tea contain:

Water . . .	10	containing	Volatile oil . . .	0·5
Extract . . .	47		Theine . . .	6·0
Exhausted leaves .	43	„	Legumin . . .	12·
	100			

100 pts. Souchong tea contain:

Water . . .	8	containing	Volatile oil . .	0·5
Extract . . .	43		Theine . . .	6·0
Exhausted leaves .	49	„	Legumin . . .	14·0
	100			

In the way in which tea is generally used, namely, as a watery infusion, the legumin remains in the spent leaves which are thrown away; but among the Mongols and other tribes of Central and Northern Asia, tea is used more as an article of food than as a mere beverage. These people make use of a product called *brick-tea*, prepared in China from inferior teas, and from the stalks and other refuse of the better sorts, which are compressed into cakes, either alone, or more frequently with addition of sheep's or bullock's blood. These cakes are pounded and boiled with water containing common salt, carbonate of potassium, or other alkaline salt (to dissolve the legumin), and the whole, mixed with fat and flour, is consumed as a thin broth.

The **tannin** of tea-leaves is commonly said to be identical with gallotannic acid. Stenhouse, however, regards it as a peculiar kind of tannin distinct from the latter; he finds also that it is associated in tea-leaves with a small quantity of gallic acid. According to R. **Wagner** also, all tannins occurring in healthy vegetable organs are essentially distinct from those which, like gallotannic acid, are found only in diseased tissues like gall-nuts (see TANNIC ACID, p. 660). The tannin of tea-leaves produces a blue-black precipitate with iron-salts.

The proportion of **ash** in unadulterated commercial tea varies from 4·73 to 6·5 per cent.; in adulterated tea it is often much larger; in some of the Chinese "Lie-teas," Warington found from 34 to 45·5 per cent. ash. The ash of tea is especially distinguished by its large amounts of iron and manganese. **Fleitmann** (Liebig's *Chemische Briefe*, 4te Aufl. ii. 182) found in an infusion of 70 grms. of Pekoe tea, 0·104 grm. ferric oxide, and 0·20 grm. manganous oxide.[*] Lehmann found in the ash of tea-infusion 0·7 per cent. manganic oxide.

The following are analyses of **tea-ash**: *a* and *b* of "*Souchong*," by Spooner; *c*, "*Oolong*," by Tevis: *d*, "*Young Hyson*," by Hague; *e*, "*Ning Young*," by Homer;[†] *f*, dry aqueous extract of tea, by Lehmann[‡]:—

	a.	*b*.	*c*.	*d*.	*e*.	*f*.
Ash per cent. of dry substance.	5·48	6·41	5·14	5·94	4·73	19·69
100 pts. of ash contain:						
$Na^{2}O$ . . .	25·46	1·70	40·00	9.26	12·88	5·03
$K^{2}O$	3·70	44·96	12·38	33·95	28·38	47·45
MgO	9·59	8·41	6·17	6·79	. .	6·84
CaO	11·36	8·77	7·68	8·17	8·39	1·24
$Fe^{2}O^{3}$ . . .	8·42	6·80	7·18	4·75	19·31	3·29
$Mn^{2}O^{3}$ . . .	. .	. .	. .	. .	. .	0·71
$P^{2}O^{5}$. . . .	12·62	11·46	8·26	16·64	17·44	9·88
SO^{3}	10·14	6·96	8·27	4·89	4·76	8·72
SiO^{2}	16·04	8·79	7·81	10·89	5·59	2·31
CO^{2}	. .	. .	. .	. .	. .	10·09
$NaCl$ . . .	2·40	2·15	2·25	4·66	3·25	3·62
	99·73	100·00	100·00	100·00	100·00	99·18

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[*] There must be some error in these numbers.

[†] The analyses *a—e* were made under Horsford's direction (Sill. Am. J. [2], xi. 249). The enormous tions in the proportions of potash and soda are probably due to defective analysis.

[‡] Liebig's *Chemische Briefe*, 4te Aufl. ii. 182.

The physiological action of tea, when used as an infusion, depends chiefly on the theine, essential oil, tannin, and inorganic constituents. In general, it may be said that tea acts upon the nervous system: when taken in moderate quantity, it heightens the activity of the brain, accelerating the flow of thought, and producing a pleasurable mental excitement; in excess it occasions sleeplessness and uneasiness, which may amount to anxiety, trembling, spasmodic attacks, &c. It, moreover, increases the action of the heart, the excretion of urea, the perspiration by the skin, and the peristallic motion of the intestines (Liebig, *Chemische Briefe*, loc. cit.). Lehmann (*Lehrb. d. physiolog. Chemie*, i. 151) also found the excretion of urea increase after taking tea; Böcker, on the other hand (Archiv. f. wiss. Heilk. 1853, i. 2), found it diminished. Further and more extended experiments are required to decide whether the use of tea accelerates or retards the change of tissue in the organism. (See Knapp's *Chemische Technologie*, 1848, ii. 84.)

TEAK. *Tectona grandis.*—The wood of this tree, which grows in the South of India and other tropical countries, frequently exhibits cracks and cavities of considerable extent, lined with a white crystalline deposit, consisting chiefly of hydrocalcic orthophosphate, $Ca''HPO^4.H^2O$, with about 11·4 per cent. ammonio-magnesian phosphate. (Abel, Chem. Soc. Qu. J. xv. 91.)

TEARS. See Serous Fluids (p. 236).

TECTIZITE. A brown mineral, supposed to be a hydrated ferrous sulphate, occurring at Schwarzenberg in Saxony, and at Bräunsdorff in the Erzgebirge, in small pyramidal and acicular crystals, and massive. Hardness = 1·5 to 2. It is easily soluble in water, and attracts moisture readily. (Dana, ii. 388.)

TECTONA. See Teak.

TEETH. (Von Bibra, Chem. Untersuch. über die Knochen u. Zähne, 1844. Frémy, Ann. Ch. Phys. [3] xliii. 47.—Hoppe, Virch. Arch. v. 170; xxiv. 13.)——The typical mammalian tooth consists of *dentine*, *enamel*, and *cement*, or *crusta petrosa*. Under the microscope, a thin section of dentine presents the appearance of a number of fine tubules, following a wavy but nearly parallel course from the pulp-cavity towards the exterior of the tooth; these tubules give off minute branches from their sides, and, as they approach the periphery, rapidly subdivide. Enamel seems to be made up of short prismatic fibres, while cement differs from bone chiefly in the absence of Haversian canals. Among the different kinds of animals, very great variations in the arrangement and relative proportion of these three constituents are observable, and the teeth of some of the lower vertebrata present special modifications of tissue known by the names of *vasodentine*, &c. &c.

Each of these dental tissues consists, like bone, of certain inorganic matters united (in a definite ratio, there is reason to believe) with an organic basis. In *cement* the organic basis is identical with that of bone. The greater part of the organic matter of dentine is also resolved by prolonged boiling into gelatin, but the proper walls of the dentinal tubules appears to be composed of a material which cannot be so resolved. The organic basis of the enamel does not yield gelatin, but seems rather to be allied to the chemical basis of epithelium.

The proportion of inorganic to organic material, and the composition of the former, will readily be seen from the following analyses. Zalesky (Hoppe-Seyler, Untersuch. i. p. 40) found in the ash of the enamel of fossil rhinoceros-tooth ·592 per cent. of fluoride of calcium. Hoppe calls attention to the analogy between the inorganic portion of enamel and apatite. The enamel of undeveloped teeth contains a form of albumin:—

Analysis of Enamel. (Hoppe.)

	Teeth of new-born infant.			Young pig.	Fossil rhinoceros.	Fossil elephant.	Mastodon.	Palæotherium.	Horse.	Dog.
Phosphate of calcium . .	67·73	75·23	76·89	82·43	85·54	82·55	85·34	86·22	84·2	89·44
Carbonate of calcium . .	8·41	7·18	6·00	8·97	7·78	8·38	11·74	9·60	9·17	5·39
Chloride of calcium . .	trace	·23	. .	·62	·65	·44	·59	·57	·66	·80
Phosphate of magnesium .	1·57	1·72	1·08	2·00	1·63	2·01	·65	1·28	1·23	4·96
Ferric phosphate . . .	. . .	·63	trace	·89	1·81	·54	·36	·76	?	
Salts soluble in water .	22·29*	·35	. .	·15	·01	trace	trace	·21	1·27	
Soluble organic matters		1·23	15·43	·71	·27	4·54	1·24*	·51		
Insoluble organic matters	. .	14·36		1·35*	2·89			1·81	3·47*	
Insoluble ferric oxide . .	. . .	. .	. .	. .	. .	. .	·09	·65		

* Determined from loss.

Comparative Analyses of Teeth and parts of Teeth of various Animals. (Von Bibra.)

	Phosphate of calcium and fluoride of calcium.	Carbonate of calcium.	Phosphate of magnesium.	Salts.	Total inorganic matter.	Fat.	Total organic matter.
Enamel:							
Woman, molar . . (27)[*]	81·63	8·88	2·55	·97	94·03	trace	5·97
Man, molar . . (28)	89·82	4·37	1·34	·88	96·41	·20	3·59
Wolf, molar . . (21)	87·82	1·21	1·10	·83	90·96	. .	9·04
Fox, molar . . (24)	88·24	1·72	1·20	·75	91·91	. .	8·09
Lion, canine . . (25)	83·33	2·94	3·70	·64	90·61	. .	9·39
Bear, canine . . (26)	84·38	2·20	6·01	·77	93·36	. .	6·64
Seal, canine . . (17)	85·60	1·94	1·00	.63	89·17	. .	10·83
Horse, molar . . (11)	89·01	1·19	1·95	·60	92·75	·19	7·25
Ox, incisor . . (6)	83·77	7·00	1·32	·61	92·70	·07	7·30
Dentine:							
Woman, molar . . (27)	67·54	7·97	2·49	1·00	79·00	·58	21·00
Man, molar . . (28)	66·72	3·36	1·08	.83	71·99	·40	28·01
Wolf, molar . . (21)	68·81	1·04	·97	·80	71·62	·73	28·38
Fox, molar . . (24)	71·84	·90	·99	·78	74·51	·40	25·49
Lion, canine . . (25)	60·03	3.00	4·21	·77	68·01	·42	31·99
Bear, canine . . (26)	64·88	1·34	6·40	·80	73·42	·82	26·58
Seal, canine . . (17)	68·46	1·09	·97	·78	71·30	·43	28·70
Elephant (Indian), tusk (14)	38·48	5·63	12·01	·70	56·82	·24	43·18
,, . . . (15)	46·48	3·86	7·84	·77	58·95	·34	41·05
Dolphin . . . (16)	66·37	1·84	1·36	·99	70·56	·82	29·44
Boar, tusk. . . (13)	60·00	2·51	6·43	·43	69·37	·13	30·63
Horse, molar . . (10)	61·28	6·08	1·75	·74	69·85	·38	30·15
Ox, incisor . . (6)	58·33	7·39	·97	·75	67·44	·52	32·56
Goat, incisor . . (3)	63·04	2·83	1·70	·93	68·50	·50	31·50
Stag, molar . . (2)	63·51	3·99	3·72	·58	71·80	·80	28·20
Crocodile . . . (29)	53·47	6·33	10·75	1·36	71·91	·77	28·09
Crusta Petrosa:							
Dolphin . . . (16)	69·42	1·79	1·47	·93	73·61	·66	26·39
Ox, incisor . . (6)	58·00	7·22	·99	·73	66·94	·95	33·06
Crocodile . . .	53·39	6·29	9·99	1·42	71·09	·76	28·91
Whole teeth:							
Saw-fish . . . (30)	61·99	3·64	1·70	1·81	69·14	1·33	30·86
Pike. . . . (31)	63·98	2·54	·73	·97	68·22	1·18	31·78
Black fish. . . (32)	59·94	9·01	2·00	1·77	72·72	2·43	27·28
Plaice . . . (33)	57·20	1·34	·88	1·82	61·24	·09	38·76

[*] The figures in parentheses are Von Bibra's numbers.

	Phosphate of calcium.	Fluoride of calcium.	Carbonate of calcium.	Sulphate of calcium.	Phosphate of magnesium.	Silica, iron, alumina, chloride of calcium, &c.	Organic substance.
Fossil teeth:							
Rhinoceros Tichorhinus:							
Upper molar:							
Enamel . . .	83·11	4·14	7·66	·95	·73	·24	3·17
Dentine . . .	54·65	3·09	12·80	. .	·80	5·63	23·03
Elephas primigenius, molar.	62·83	4·15	14·99	. .	2·11	·32	15·60
,, ,, ,, .	68·43	3·72	15·46	. .	1·34	1·91	9·14
Cave Bear, molar . .	64·03	2·51	1·46	. .	8·25	·30	23·45
Fish, *acrodus* . .	. .	90·01	1·80	. .	·52	5·50	2·17
Fish from chalk .	. .	85·01	9·11	. .	·45	14·89	·54 (Loss)

TEKORETIN. A resin found in fossil pine-stems in the bogs of Holtegaard in Denmark. It crystallises in large prisms, melting at 45°, insoluble in water, slightly soluble in alcohol, very soluble in ether. It distils without alteration near the boiling-point of mercury. Chlorine converts it into a crystalline substance. Nitric acid transforms it into oxalic acid and a brown resin, apparently containing nitrogen. It gave, as the mean of four analyses, 87·17 per cent. carbon and 12·84 hydrogen, agreeing approximately with the formula nC^5H^8. (Forchhammer, Ann. Ch. Pharm. xli. 39.)

TELAESIN or **TELESCIN.** A product formed, according to Rochleder (J. pr. Chem. lxxxvii. 22), by the action of aqueous acids or alkalis on argyræscin, aphrodæscin, and æscinic acid, constituents of the cotyledons of horse-chestnut seeds (iii. 172).

TELERYTHRIN. A product of the decomposition of orsellinic ether (iv. 236), formed, according to Kane (Ann. Ch. Pharm. xxxix. 36), when the ether dissolved in hot water is exposed to the air for several months; it is probably a mixture, chiefly consisting of orcin and erythromannite.

TELESIE. Syn. with Corundum (ii. 86).

TELLURAMYL. See Amyl, Telluride of (i. 206).

TELLURATES. See Tellurium, Oxides and Oxygen-acids of.

TELLURETHYL. See Ethyl, Telluride of (ii. 550).

TELLURHYDRIC ACID. H^2Te. See Hydrogen, Telluride of (iii. 204).

TELLURIC ACID. See Tellurium, Oxides and Oxygen-acids of.

TELLURIC BISMUTH. See Tellurides.

TELLURIC OCHRE. Native tellurous oxide.

TELLURIC SILVER. See Tellurides.

TELLURIDES and **TELLURHYDRATES.** Compounds analogous to the sulphides and sulphydrates, and to the selenides and selenhydrates. The tellurides belong to the class of metallic alloys: those of bismuth, gold, lead, and silver are found native; the others may be obtained by fusing the respective metals with tellurium, or (in the wet way) by precipitating solutions of the metals with tellurhydric acid or an alkaline tellurhydrate. The tellurides of potassium and sodium are prepared by heating powdered tellurium with an alkaline carbonate, containing finely-divided charcoal—black flux, for instance. The access of air to the mass must be prevented till it is quite cold, on account of its highly pyrophoric nature. It may then be exhausted with water in which the alkaline tellurides dissolve, being probably converted into tellurhydrates. They may also be formed by passing tellurhydric acid gas through solutions of caustic alkali. Tellurhydrate solutions have a portwine-colour, and deposit tellurium on exposure to the air.

Telluride of Bismuth.—This alloy occurs native in several localities, forming the mineral called *Telluric Bismuth*, *Tetradymite*, or *Bornite*. Some specimens contain only bismuth and tellurium, but generally the tellurium is partly replaced by sulphur and selenium. It forms crystals belonging to the hexagonal system, namely acute rhombohedrons, having the angles of the terminal edges = 66° 40′, combined (according to Haidinger) with the basal face oR, and aggregated in cruciform groups of four individuals. It cleaves perfectly parallel to the base, and thin laminæ are more or less flexible, also somewhat elastic. The mineral likewise occurs in granulo-laminar masses. Hardness = 1 to 2. Specific gravity = 7·2 to 7·9. Before the blowpipe it melts with tolerable facility, coating the charcoal with a yellow-and-white deposit, the reaction varying in character according to the proportion of sulphur or selenium present. It dissolves in nitric and in sulphuric acid.

The variations in composition of this mineral will be seen from the following analyses *:—

	Virginia.				Georgia.			N. Carolina.	Cumberland.
	Genth.				Genth.		Jackson	Genth.	Rammelsberg.
Bismuth	53·0	53·8	51·5	. .	50·8	50·97	79·1	61·3	84·33
Tellurium	48·2	47·0	49·8	46·1	48·2	47·25	18·0	33·8	6·73
Sulphur	. .	. .	. .	0·3	. .	. .	. .	5·2	6·43
Selenium	. .	trace	. .	. .	trace	trace	1·2	trace	
	101·2	100·8	101·3	. .	99·0	98·22	98·3	100·3	97·49

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* Berzelius, Pogg. Ann. i. 271.—Damour, Ann. Ch. Phys. [3] xiii. 372.—Genth, Sill. Am. J. [2] xvi. 81; xix. 15.—Hruschauer, J. pr. Chem. xlv. 456.—Jackson, Sill. Am. J. [2] vi. 188; x. 73.—Rammelsberg, *Mineralchemie*, p. 5.—Wehrle, Pogg. Ann. xxi. 595.

	Schoul-Kau in Hungary.			Pilsen in Hungary.	Brazil.	
	Wehrle.	Berzelius.	Hruschauer.	Wehrle.	Damour.	
Bismuth	60·0	58·3	59·2	61·1	79·1	78·4
Tellurium	34·6	36·0	35·8	29·7	15·9	15·6
Sulphur	4·8	4·3	4·6	2·3	3·1	4·5
Selenium	. .	. .	. .	. .	1·5	
	99·4	98·6	99·6	93·1	99·6	98·5

The great variations in the proportion of tellurium to bismuth, and the fact that the crystalline forms of the mineral and its two constituents belong to the same system (bismuth, rhombohedral; tellurium, hexagonal), lead to the conclusion that it is not a definite compound, but an isomorphous mixture of tellurium and bismuth. It must be observed, however, that many of the analyses—namely, those by Genth of the specimens from Virginia and Georgia, which contain no sulphur and little or no selenium—agree nearly with the formula Bi^2Te^3 (requiring 59·9 per cent. bismuth, and 48·1 tellurium); and that those by Berzelius, Wehrle, and Hruschauer may be represented approximately by Bi^2Te^2S.

Telluride of Gold and Silver. See SYLVANITE (p. 647).

Telluride of Hydrogen. See HYDROGEN, TELLURIDE OF (iii. 204).

Telluride of Lead, PbTe. *Altaite. Cubic Tellurium.*—This mineral occurs in the mine of Savodinskoi, near Barnaoul in the Altai, usually massive, with cubic cleavage, rarely in cubic crystals. It has a metallic lustre and tin-white colour, like that of native antimony. Hardness = 3 to 3·5. Specific gravity = 8·159. Sectile. Before the blowpipe it volatilises in the reducing flame, leaving only a minute bead of silver, and colours the flame blue. It is soluble in nitric acid. It contains 38·37 per cent. tellurium, 60·35 lead, and 1·28 silver (G. Rose, Pogg. Ann. xviii. 68), and is therefore PbTe (38·3 tellurium, and 61·7 lead), mixed with a small quantity of silver-telluride.

Telluride of Silver, Ag^2Te. *Hessite. Petzite. Bitellurct of Silver.*—Occurs in the Savodinskoi mine in the Altai, at Nagyag in Transylvania, and at Retzbanya in Hungary, in coarse-grained masses and granular, with metallic lustre, lead-grey or steel-grey colour, and slightly malleable. Hardness = 2 to 3·5. Specific gravity = 8·3 to 8·9. Before the blowpipe on charcoal, it melts to a black globule, which on cooling, after being subjected to the action of the reducing flame, exhibits points or dendrites of silver on its surface. Heated in a tube, it melts, and colours the glass yellow. Fused with carbonate of sodium, it yields a globule of pure silver.

Analyses:—a, b. From the Savodinskoi mine (G. Rose, Pogg. Ann. xviii. 64).—*c.* From Nagyag (Petz, *ibid.* lvii. 470).—*d, e.* From Retzbanya (Rammelsberg, *Mineralchemie,* p. 15): *d.* massive; *e.* granular with green coating; after deduction of 15·25 per cent. insoluble matter:

	a.	*b.*	*c.*	*d.*	*e.*
Tellurium	36·96	36·89	37·76	. .	33·0
Silver	62·42	62·32	61·55	60·28	64·5
Gold	. .	. .	0·69		
Iron	0·24	0·50			
	99·62	99·71	100·00	. .	97·5

The formula Ag^2Te requires 37·27 per cent. tellurium, and 62·73 silver.

Tellurides, Organic. See AMYL, ETHYL, METHYL, TELLURIDES OF (i. 206; ii. 550; iii. 992).

The alcoholic tellurides obtained by Wöhler have the composition R^2Te.—Cahours has lately shown (Compt. rend. lx. 20, 1147; Jahresb. 1865. p. 447), that telluride of methyl unites directly with iodide of methyl, forming a crystalline compound, $(CH^3)^3TeI$, sparingly soluble in water, easily soluble in alcohol. This iodide, treated with oxide of silver, yields an alkaline product, which, when neutralised with hydrochloric acid, forms with platinic chloride, an orange-coloured double salt, $2(CH^3)^3TeCl.Pt^{iv}Cl^4$.

Telluride of ethyl unites in like manner with iodide of ethyl, forming the compound $(C^2H^5)^3TeI$; and corresponding compounds are formed by the sulphides and selenides of ethyl and methyl with the iodides of those radicles.

TELLURITES. See TELLURIUM, OXIDES AND OXYGEN-ACIDS OF.

TELLURIUM. *Symbol*, Te. *Atomic Weight*, 128. *Vapour-density*, obs. at 1390° = 9·00; calc. (1 vol.) = 8·86.

This element, though decidedly metallic, must be classed as a member of the sulphur family, as it approximates very closely in its chemical characters to sulphur, and still more to selenium. It was first identified as a distinct metal by Klaproth, in 1798, who gave it the name "tellurium," from *tellus*, the mythological name of the earth.

Tellurium is one of the rarer elements, being found in a few localities only, chiefly in Hungary and Transylvania, in the silver mine of Savodinskoi in the Altai, and in the State of Virginia. It occurs native in a state of considerable purity: a specimen from Nagyag was found by Petz to contain 97·22 per cent. tellurium and 2·78 gold; and Klaproth found in a specimen from the Maria Loretto mine, near Zalathna in Hungary, 92·53 tellurium, 0·25 gold, and 7·20 iron. The principal ores of tellurium are the tellurides of bismuth, lead, gold, and silver, already described (iv. 1; v. 707, 708).

Preparation.—Tellurium is separated from its ores by processes analogous to those which yield selenium (p. 221).—1. Native telluride of bismuth, freed as far as possible from its matrix, and made into a paste with pearlash and oil, is gradually raised in a covered crucible to a full white heat; and the fused mass when cold is treated with boiling water, which extracts telluride of potassium, forming a portwine-coloured solution, from which the tellurium is deposited in metallic scales, by passing a current of air through it, or by mere exposure to the air.—2. Finely pulverised foliated tellurium, or nagyagite (iv. 1), freed from sulphides of lead and antimony by repeated boiling with hydrochloric acid, and washing with water, is heated with strong nitric acid, whereby tellurous acid is obtained in solution. This is evaporated to dryness, and the residue, after solution in hydrochloric acid, is reduced by a current of sulphurous acid gas. For further details, see *Gmelin's Handbook*, iv. 393.

Properties.— Tellurium is a tin-white, shining, brittle metal, having a great tendency to crystallise. The crystals belong to the hexagonal system. Native tellurium occurs in rhombohedral crystals, isomorphous with those of antimony, arsenic, and bismuth, and exhibiting the faces R, with those of derived rhombohedrons; also oR and ∞R. Length of principal axis, for R = 1·3298; angle R : R in the terminal edges = 86° 57′. The opposite rhombohedrons +R and −R likewise occur together, forming a hexagonal pyramid (in combination with ∞P and oP), in which the angle P : P in the terminal edges = 130° 28′; in the lateral edges = 113° 52′. Cleavage perfect parallel to ∞R; in traces parallel to oR. According to H. Rose, tellurium separates from a solution of potassium-telluride, by spontaneous decomposition, in six-sided prisms with rhombohedral summits.

Tellurium conducts heat and electricity, though not very readily. Its specific gravity is 6·1 to 6·33; hardness of the native metal = 2 to 2·5. It melts at about 500°, volatilises at a higher temperature, and condenses in crystalline needles, or in drops. It may be purified by distillation in a current of hydrogen. Its vapour-density, as determined by Deville and Troost (Jahresb. 1863, p. 17), is 9·00 at 1390°, and 9·08 at 1439°. The vapour has a greenish-yellow colour, like that of chlorine-gas.

Tellurium, when strongly heated in the air, takes fire, burns with a lively blue flame edged with green, producing white fumes of tellurous acid, and emitting a peculiar odour, often partly due to the presence of traces of selenium. (Respecting the spectrum of its flame, see J. Werther, J. pr. Chem. lxxxviii. 180; Jahresb. 1863, p. 235).—Tellurium, like sulphur and selenium, dissolves to a slight extent in cold strong sulphuric acid, and is precipitated unchanged on dilution with water; but when heated with strong sulphuric acid, it is oxidised and dissolved as tellurous acid, while sulphurous anhydride is evolved as gas.—By strong *nitric acid*, it is quickly converted into tellurous acid.—*Hydrochloric acid* has no action upon it; but with *nitromuriatic acid*, it yields tellurous mixed with telluric acid.—By fusion with *saltpetre*, it yields tellurate of potassium.—Strong *potash-ley* dissolves tellurium at the boiling heat, forming a red liquid, containing telluride and tellurite of potassium. On cooling, or on dilution with water, however, the red colour disappears, and tellurium is separated, in consequence of the reducing action exerted by the potassium on the tellurous acid:

$$2K^2Te + K^2TeO^3 = 3K^2O + Te^3.$$

Tellurium, fused with *carbonate of potassium*, likewise yields a mixture of telluride and tellurite.

Tellurium, in its chemical relations, bears a very close analogy to sulphur and selenium. It forms two oxides—namely, tellurous oxide, TeO^2, and telluric oxide, TeO^3—which, in combination with water and with metallic bases, yield acids and salts analogous to those formed by the corresponding oxides of sulphur and selenium.—

With *hydrogen*, it forms a gaseous compound, H^2Te, analogous to sulphydric and selenhydric acids. It unites also with the *alcohol-radicles*, methyl, ethyl, and amyl, forming compounds represented by the general formula R^2Te, which are diatomic radicles, analogous to the selenides of the alcohol-radicles.—With *chlorine* it forms a tetrachloride, $TeCl^4$, analogous to $SeCl^4$, and a dichloride, $TeCl^2$, to which there does not appear to be any definite analogue among the sulphur- and selenium-compounds (pp. 223, 533); and similar compounds with *bromine* and *iodine*. The inorganic compounds of tellurium have been studied chiefly by Berzelius; the organic compounds by Wöhler.

TELLURIUM, ALLOYS OF. See TELLURIDES (p. 707).

TELLURIUM, BROMIDES OF. The dibromide, $TeBr^2$, is produced by distilling the tetrabromide with finely pulverised tellurium, and passes over as a violet vapour, which condenses to slender black needle-shaped crystals. It melts easily, and is decomposed by water with formation of tellurous acid. (Berzelius.)

The *tetrabromide*, $TeBr^4$, may be prepared by adding finely divided tellurium, with frequent agitation, to bromine contained in a tube cooled with ice, and distilling off the excess of bromine after all the tellurium is dissolved (Berzelius). According to v. Hauer (J. pr. Chem. lxxiii. 98), it is more easily prepared by covering small pieces of tellurium with hydrobromic acid in a flask, then adding bromine, and leaving the flask closed till all the bromine has disappeared, the action being assisted by shaking the flask from time to time. The ruby-coloured solution thus obtained yields the dry compound by evaporation over the water-bath.

Tetrabromide of tellurium forms a compact red-yellow mass, which melts at a gentle heat to a dark-red transparent liquid, and solidifies in the crystalline form on cooling. It may be sublimed without decomposition in pale-yellow needles. It dissolves without alteration in a small quantity of water, forming a yellow solution, which becomes colourless on dilution, the tetrabromide being thereby resolved into hydrobromic and tellurous acids. The yellow solution evaporated over the water-bath deposits the hydrated tetrabromide in ruby-coloured crystals.

Tetrabromide of tellurium forms cinnabar-red compounds with the bromides of the alkali-metals.—The *potassium-salt*, $2KBr.TeBr^4.3H^2O$, was first obtained by Berzelius, by evaporating a mixed solution of the component salts. According to v. Hauer, it is better prepared by mixing 1 at. finely pulverised tellurium with 2 at. bromide of potassium in a flask, and adding water till the bromide is completely dissolved; then adding bromine by small portions, with frequent agitation, and leaving the flask closed till all the bromine has disappeared. On warming the resulting dark-red solution, to expel the excess of bromine, decanting it from a yellowish deposit which forms, and leaving it to cool, the double salt separates in dark-red, opaque, shining crystals, which effloresce superficially in dry air. It is slightly soluble in cold, easily in hot water. When heated, it gives off its water of crystallisation without melting. The anhydrous salt, which is orange-yellow, decomposes at a higher temperature, giving off tetrabromide of tellurium.

TELLURIUM, CHLORIDES OF. The dichloride, $TeCl^2$, is formed by distilling a mixture of equal parts of finely divided tellurium and the tetrachloride (Berzelius), or by passing chlorine slowly over strongly heated tellurium, or native telluride of silver. It may be freed from admixed tetrachloride by fractional distillation (H. Rose). It is a black amorphous mass, having an earthy fracture; melts easily to a black liquid, and is much more volatile than the tetrachloride. Its vapour is purple when mixed with air; yellow when pure. When exposed to the air, it absorbs moisture, but does not fume. When mixed with water, it becomes milky from formation of tellurous acid. Hydrochloric acid decomposes it, separating half the tellurium in the metallic state, and dissolving the other half as tellurous acid. The dichloride may be fused in all proportions with metallic tellurium, or with the tetrachloride.

Tetrachloride of Tellurium, $TeCl^4$, is obtained by gently heating tellurium in a stream of chlorine-gas, till a dark-yellow liquid is produced. This liquid turns yellow on cooling, and crystallises to a white mass at the moment of solidification. The tetrachloride melts easily to a yellow liquid, turning red near its boiling point: it is not very volatile, but forms a dark-yellow vapour when strongly heated. It is very deliquescent, and is decomposed by cold water, with separation of a basic salt and tellurous acid. Boiling water dissolves it, the solution on cooling depositing crystals of tellurous acid. Dilute hydrochloric acid dissolves it without alteration.

By mixing a solution of the tetrachloride with *chloride of ammonium* or *chloride of potassium*, double salts are formed, which crystallise in lemon-yellow octahedrons.—A compound of the tetrachloride with *chloride of aluminium*, $2AlCl^3.TeCl^4$, is obtained, to R. Weber (J. pr. Chem. lxxvi. 313), by melting the two chlorides together, and expelling any excess of aluminium-chloride that may be present by gentle heating. This double chloride is a yellowish-white, easily fusible mass, very soluble in dilute sulphuric acid. When heated nearly to its boiling-point, which is very high, it is partially decomposed, leaving a residue richer in tellurium.

Tetrachloride of tellurium quietly absorbs *ammonia-gas* at ordinary temperatures, swelling up, and changing to a greenish-yellow mass of the compound $4NH^3.TeCl^4$. This compound is permanent in the air, but is decomposed by water into tellurous acid and sal-ammoniac. When heated, it gives off sal-ammoniac, hydrochloric acid, and nitrogen-gas, while tellurium is separated. (Espenschied, J. pr. Chem. lxxx. 480.)

TELLURIUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe reactions.*—All compounds of tellurium are easily reduced on *charcoal* in the inner flame, the reduced metal being volatilised, and forming a white deposit of tellurous oxide on the charcoal. With *borax* and *microcosmic salt*, tellurous oxide gives a clear colourless bead, which, when heated on charcoal, is rendered grey and opaque by the reduced metal. The oxides of bismuth and antimony, when reduced on charcoal in the inner flame, also give white incrustations, which may be confounded with tellurous oxide. Antimonious oxide, however, when heated in the inner flame, gives a bluish tinge, whereas tellurous oxide gives a fine green colour to the outer flame. Moreover tellurous oxide, when heated in a tube open at both ends, volatilises entirely, forming, on the cool part of the tube, a white sublimate, which, by careful heating, may be fused to colourless drops. Antimonious oxide, on the other hand, is only partially volatilised, being partly converted into the non-volatile oxide, SbO^2; the sublimate may be driven from one part of the tube to another by heat, but does not fuse into drops. Bismuth-oxide similarly treated gives scarcely any sublimate, but melts to a dark-brown liquid, which becomes pale-yellow on cooling, and corrodes the glass. From selenium, which it resembles more closely than any other element, tellurium is distinguished by the odours emitted when the compounds of the two elements are heated on charcoal before the blowpipe, pure tellurium emitting only a slightly acid odour, whereas selenium emits a powerful odour of decayed horse-radish: traces of selenium existing in tellurium-compounds are easily detected in this manner (p. 224).

2. *Reactions in Solution.*—All native tellurium-compounds are insoluble in water, but soluble in nitric acid. Among the artificially prepared compounds, the tellurites of the alkali-metals, and also the tellurates (in the hydrated state) are easily soluble in water; the tellurites and tellurates of the other metals are insoluble or sparingly soluble in water, but for the most part soluble in hydrochloric acid. The tellurides of the alkali-metals are also soluble in water, and their solutions, when exposed to the air, decompose quickly, with separation of metallic tellurium. Tellurous acid (hydrated tellurous oxide) dissolves easily in acids; the solution in nitric acid gradually deposits anhydrous telluric oxide. In solutions not containing too great an excess of acid, especially in the hydrochloric acid solution, water throws down a precipitate of tellurous acid. The hydrochloric acid solution of tellurous oxide is yellow. Telluric acid is distinguished from tellurous acid by its greater solubility in water. The salts of the two acids are distinguished from one another by the fact that the tellurates, when heated with hydrochloric acid, give off chlorine, which is not the case with the tellurites. Moreover, the solutions of tellurates in hydrochloric acid are colourless, and are not precipitated by water like those of the tellurites, even when there is but little free hydrochloric acid present.

Sulphydric acid produces immediately, in acid solutions of tellurous oxide, a brown precipitate of tellurium-sulphide, easily soluble in sulphide of ammonium; in acid solutions of telluric oxide, the same precipitate is formed after the liquid has stood for some time in a closed vessel, and in a warm place. The colour of this precipitate distinguishes it from all other metallic sulphides which are soluble in sulphide of ammonium (that of selenium is reddish-yellow) except stannous sulphide; but solutions of stannous salts are easily distinguished from those of tellurium-salts by their reaction with chloride of gold, tellurium-solutions not forming with this reagent any precipitate resembling the purple of Cassius; moreover, solutions of tellurous oxide yield, with ammonia and alkaline carbonates, a white precipitate easily soluble in excess of the alkaline reagent, whereas the precipitates formed in like manner with stannous salts are insoluble in excess. Solutions of telluric oxide give no precipitate with alkalis.

Sulphurous acid and *alkaline sulphites* produce, in acid solutions of tellurous or telluric oxides, after some time in the cold, or immediately on heating, a black precipitate of metallic tellurium. A similar precipitate is formed by solution of *stannous chloride* and by metallic *zinc*. The precipitate of selenium formed by the same reagents in a solution of selenious acid is red. The precipitated tellurium may also be distinguished from selenium by its reaction with solution of *potassium-cyanide*, which dissolves selenium but not tellurium; further by its behaviour before the blowpipe (p. 711); and lastly, by dissolving the precipitate in nitric acid, nitromuriatic acid, or a mixture of hydrochloric acid and potassium-chlorate, neutralising the solution, after complete oxidation, with carbonate of sodium, evaporating to dryness, fusing the residue at a moderate heat with nitre, dissolving the product in water, acidulating with nitric acid, and adding chloride of barium. Selenate of barium is then precipitated, whereas tellurate of barium remains in solution.

3. *Estimation and Separation.*—Tellurium is mostly estimated in the metallic state. If it is present in solution in the form of tellurous acid, as is always the case when tellurium-ores are treated with nitric acid, it is best precipitated by *sulphurous acid* or an *alkaline sulphite.* The tellurium thereby separated is collected on a weighed filter, carefully dried at a gentle heat, and weighed. If the tellurous acid is combined with bases in such proportion that the solution does not exhibit an acid reaction, it must be mixed with hydrochloric acid in sufficient quantity to redissolve the precipitate of tellurous acid formed at first. It is best also to concentrate the liquid as much as possible before adding the reducing agent, as the tellurium is then separated more quickly and completely than from a more dilute solution. The solution thus prepared is to be heated in a flask, but not to the boiling-point, and the solution of alkaline sulphite gradually added: the tellurium is then precipitated as a black bulky powder. Nitric acid, if present, may vitiate the result by reoxidising part of the reduced tellurium: it should therefore be previously removed by warming the liquid with hydrochloric acid. If the tellurium is present as telluric acid, the latter must first be reduced to tellurious acid by heating the solution with hydrochloric acid as long as chlorine continues to escape.

The method of reduction by sulphurous acid or alkaline sulphites, serves to separate tellurium from the tellurites and tellurates of the alkali-metals, and of other metals which are not precipitated by sulphydric acid. If the quantity of alkali-metal is to be likewise estimated, the reduction must of course be effected by sulphite of ammonium or free sulphurous acid; in the latter case, the solution must be digested for some days with excess of aqueous sulphurous acid, in a closed vessel placed in a warm situation. The separation of tellurium from the tellurites and tellurates of these metals may also be effected by precipitation with *sulphydric acid.* As the precipitated tellurium-sulphide is generally mixed with free sulphur, it must be digested, while still moist, with nitromuriatic acid, or better, with hydrochloric acid and potassium-chlorate, and the tellurium precipitated from the filtered solution by an alkaline sulphite, as above. Telluric acid must first be reduced to tellurous acid by heating with hydrochloric acid.

From the tellurites and tellurates of metals which are precipitated by sulphydric acid, and form sulphides insoluble in sulphide of ammonium, tellurium may be separated by supersaturating the solution with ammonia, and digesting it at a very gentle heat with excess of *ammonium-sulphide.* The sulphide of tellurium then remains dissolved, and may be precipitated from the filtered solution by acetic or very dilute hydrochloric acid, oxidised as above with nitromuriatic acid, &c., and the tellurium precipitated by an alkaline sulphite. The same method may be used for separating tellurium from iron, cobalt, nickel, zinc, and manganese. It is, however, not so advantageous in any case as the precipitation with alkaline sulphites, because it is difficult to ensure the complete solution of the tellurium-sulphide in sulphide of ammonium.

From all metals which form non-volatile chlorides, tellurium may be separated by igniting the compound in a stream of *chlorine*, whereby it is volatilised as dichloride or tetrachloride, according to the rapidity of the stream of gas. The volatilised chloride is passed into water acidulated with hydrochloric acid, in which the tetrachloride of tellurium dissolves completely, the dichloride with separation of tellurium. The tellurium is then reduced from the solution by an alkaline sulphite.

Another method of separation, applicable in most cases, is to fuse the compound with 3 pts. dry sodium-carbonate and 3 pts. sulphur in a covered crucible, and digest the mass when cold with water. The metals combined with the tellurium then remain as insoluble sulphides, while the tellurium dissolves as sulphotellurite of sodium. From this solution the tellurium-sulphide may be precipitated by a dilute acid, and treated as above for the determination of the tellurium.

From antimony, arsenic, and tin, tellurium may be separated by precipitation with *alkaline sulphites.*

From selenium and sulphur it is separated by fusion with *potassium-cyanide*, in the manner already described under SELENIUM (p. 225).

4. *Atomic Weight of Tellurium.*—Berzelius (Pogg. Ann. xxviii. 392) determined the atomic weight of tellurium by ascertaining the increase of weight of the

metal when converted into tellurous oxide by oxidation with nitric acid. In three experiments,

	1·2725 grms.	1·5715 grms.	2·88125 grms. tellurium
yielded	1·5895 „	1·9365 „	3·6000 grms. TeO^2;
whence Te =	128·41	128·29	128·27,

or, as a mean result, 128·34. Berzelius, however, gives the preference to the second and third experiments, which give Te = 128.

Von Hauer (Wien. Akad. Ber. xxv. 135), by precipitating bromide of tellurium and potassium, $2KBr.TeBr^2$, with nitrate of silver, obtained, as a mean of five closely agreeing experiments, 69·924 per cent. bromine; whence (if Ag = 108·1, Br = 80, K = 39·2), the atomic weight of tellurium is found to be 128·06.

Dumas (Ann. Ch. Pharm. cxiii. 30), from experiments not yet published in detail, concludes that Te = 159.

TELLURIUM, FLUORIDE OF, Te^4.—Produced by dissolving tellurous oxide in hydrofluoric acid. The solution evaporated over the water-bath leaves a colourless syrup, which on cooling deposits milk-white nodules, probably an oxyfluoride.

TELLURIUM, IODIDES OF. The *di-iodide*, TeI^2, is produced by gently heating tellurium with iodine. The excess of iodine then volatilises, leaving the compound in shining black crystalline flocks. It is easily fusible, and gives off iodine when strongly heated. Water has no action upon it. (Berzelius.)

The *tetra-iodide*, TeI^4, obtained by digesting finely pulverised tellurous oxide with hydriodic acid, forms soft black granules, which stain the fingers. It is very unstable, and melts, with evolution of iodine, when heated. With boiling water it forms a dark-brown solution, while a grey-brown oxyiodide remains undissolved. The tetra-iodide dissolves in hydriodic acid, and the solution, when evaporated, deposits colourless metallic-shining prisms, probably a compound of the tetra-iodide with hydriodic acid.

By saturating the solution of the tetra-iodide in hydriodic acid with an alkali, double iodides are obtained, which separate, by spontaneous evaporation, in iron-grey metallically lustrous crystals.

The *hexiodide*, TeI^6, is perhaps contained in the brown solution of telluric oxide in hydriodic acid.

TELLURIUM, OXIDES AND OXYGEN-ACIDS OF. Tellurium forms two oxides, TeO^2 and TeO^3, which unite with bases forming salts analogous to the sulphites and sulphates.

Tellurous Oxide or **Anhydride,** TeO.—This oxide is produced when tellurium burns in the air. It may also be obtained by exposing the corresponding hydrate (tellurous acid) to a gentle heat, and separates from the aqueous solution of the hydrate when heated to 40°. The same change takes place spontaneously, though more rapidly on the application of heat, in the nitric acid solution of tellurous acid obtained by dissolving tellurium in nitrous acid: in this case the deposit of tellurous oxide is much more abundant, and, if slowly produced, is distinctly crystalline, showing here and there well-defined octahedrons. The mineral called tellurite or telluric ochre, occurring at Facebay, near Zalathna in Transylvania, in small greyish-yellow spherules, imbedded in quartz together with tellurium, exhibits, according to Petz (Pogg. Ann. lvii. 478), the reaction of tellurous oxide before the blowpipe.

Tellurous oxide is slightly soluble in water, but has no action upon litmus. It is fusible and volatile. The fused oxide is a transparent deep yellow liquid, which solidifies on cooling to a white highly crystalline mass. When fused with alkaline hydrates or carbonates, it forms tellurates.

TELLUROUS HYDRATE OR TELLUROUS ACID, $H^2TeO^3 = H^2O.TeO^2$.—This acid is best obtained by decomposing tetrachloride of tellurium with water:

$$TeCl^4 + 3H^2O = 4HCl + H^2TeO^3.$$

It may be prepared from tellurite of potassium or sodium, by adding nitric acid till a distinct acid reaction is produced; also by dissolving tellurium in dilute nitric acid of specific gravity 1·25, and pouring the solution, after the lapse of not more than a few minutes, into an excess of water. If the precipitation be delayed for a longer time, the anhydrous oxide is thrown down instead of the hydrate.

Tellurous acid, prepared by either of these processes, is a somewhat bulky precipitate, which, when dried over oil of vitriol, forms a light white earthy powder, having a bitter metallic taste. It is slightly soluble in water, especially when recently precipitated. It dissolves both in acids and in alkalis.

The solutions of tellurous hydrate in acids are all stable, with the exception of the nitric acid solution, which, as already observed, deposits telluric oxide. They do not, however, yield definite salts on evaporation, excepting the phosphoric acid solution, which deposits a white powder, and the oxalic acid solution, which deposits crystalline grains, soluble without decomposition in water.—A *sulphate of tellurium*, ($Te^{iv}S^2O^6$), is formed by gently heating finely pulverised tellurium with oil of vitriol. (See SULPHATES, p. 614.)

The solution of tellurous hydrate in hydrochloric acid is decomposed by *water*, if not very strongly acid, depositing tellurous hydrate.—*Alkalis* and *alkaline carbonates* also form a white precipitate of tellurous hydrate, soluble in excess of the alkaline reagent. —*Chloride of barium* forms a white precipitate, insoluble in ammonia.—The reactions with *sulphydric acid*, *sulphide of ammonium*, *sulphurous acid*, *alkaline sulphites*, *stannous chloride*, and *zinc*, have been already described; also the blowpipe-reactions of tellurous oxide (p. 711).

TELLURITES.—Tellurous acid forms, with the *alkali-metals*, neutral and acid salts analogous to the sulphites and selenites; also hyperacid salts; viz.:

$$\begin{array}{lll} \text{Neutral Tellurites,} & M^2TeO^3 = M^2O.TeO^3. \\ \text{Acid} \quad ,, & MHTeO^3, \text{ or } M^2O.H^2O.2TeO^2. \\ \text{Hyperacid} \quad ,, & \left.\begin{matrix} MHTeO^3 \\ H^2TeO^3 \end{matrix}\right\}, \text{ or } M^2O.3H^2O.4TeO^2. \end{array}$$

There are also anhydrous ditellurites of alkali-metal, such as $K^2O.2TeO^2$, or $K^2TeO^3.TeO^2$.—With the *alkaline earth-metals*, tellurous acid forms anhydrous mono-, di-, and tetra-tellurites, represented by the formulæ, $M''O.TeO^2$, $M''O.2TeO^2$, and $M''O.4TeO^2$.—With the *heavy metals* it appears to form only neutral salts.

The tellurites of alkali-metal are formed by direct combination, either in the dry or in the wet way; the rest either by fusing tellurous oxide with the respective bases, or by precipitation. The neutral and acid tellurites of alkali-metal are soluble in water; the tellurites of the alkaline earth-metals are slightly soluble; and those of the earth-metals and heavy metals are insoluble. Most tellurites are soluble in hydrochloric acid. The solutions are yellow, and do no not give off chlorine when heated, a character by which the tellurites are distinguised from the tellurates. If the quantity of hydrochloric acid present in these solutions is not very great, they deposit tellurous acid on dilution with water; this precipitation is, however, prevented by the presence of tartaric acid. Tellurites are mostly fusible, and solidify to a crystalline mass on cooling; the hyperacid tellurites of alkali-metal form colourless glasses after fusion. Most tellurites, when ignited with charcoal and potash, yield tellurite of potassium, which dissolves with portwine-colour in water.

Tellurite of Aluminium is a white flocculent precipitate.

Tellurite of Ammonium.—A solution of tellurous acid in ammonia gives off ammonia by evaporation, even at a very gentle heat, and yields a precipitate of tellurous acid.—According to Flückiger (Jahresb. 1862, p. 173), tellurite of ammonium is produced by heating tellurium with aqueous ammonia in sealed tubes.—The *hyperacid salt*, $(NH^4)^2O.4TeO^2.4H^2O$, or $(NH^4)HTeO^3.H^2TeO^3.3\frac{1}{2}H^2O$, is formed by dissolving tellurous acid or tetrachloride of tellurium in warm aqueous ammonia, and separates, on adding a little sal-ammoniac to the cooled solution, as a heavy white granular precipitate; a further quantity may be precipitated from the filtrate by alcohol. It is resolved by heat into ammonia, water, and tellurous oxide. (Berzelius.)

Tellurites of Barium.—The *neutral salt*, $Ba''TeO^3 = Ba''O.TeO^2$, is produced by fusing 1 at. tellurous oxide with 1 at. barium-carbonate, and solidifies, on cooling, to a colourless crystalline mass; by double decomposition it is obtained as a white, bulky, flocculent precipitate. It is sparingly soluble in water, the solution when exposed to the air depositing carbonate and tetratellurite of barium.

The *tetratellurite*, $Ba''O.4TeO^2 = Ba''TeO^3.3TeO^2$, prepared by fusing 4 at. tellurous oxide with 1 at. barium-carbonate, solidifies to a transparent colourless glass. It is also produced by mixing the aqueous solution of the neutral salt with very dilute nitric acid, and then separates in bulky flakes.

Tellurite of Cadmium is a white gelatinous precipitate, which dries up to a brittle mass, having a conchoïdal fracture. It dissolves in hydrochloric and in nitric acid. Ammonia added to these solutions, throws down cadmium-oxide; sulphydric acid and sulphide of ammonium produce in the cold a brown-red precipitate of cadmium-sulphotellurite. (Oppenheim.)

Tellurites of Calcium.—The *neutral salt*, $Ca''TeO^3$, produced by heating 1 at. tellurous oxide with 1 at. lime, forms a white mass, which remains solid at the melting-point of silver. By precipitation, it is obtained in white flocks, slightly soluble in cold, more soluble in hot water.—The *ditellurite*, $Ca''O.2TeO^2 = Ca''TeO^3.TeO^2$, melts only at a white heat, and solidifies on cooling to an opaque mass, consisting of micaceous scales.—The *tetratellurite*, $Ca''O.4TeO^2 = Ca''TeO^3.3TeO^2$, fuses more easily, giving off fumes of tellurous oxide, and likewise solidifies in micaceous scales. (Berzelius.)

Tellurite of Chromium is a grey-green precipitate, soluble in excess of the chromic salt.

Tellurite of Cobalt is a dark-purple precipitate.

Tellurite of Copper, obtained by precipitation, is a siskin-green powder, insoluble in water; when heated, it gives off water and turns black, melts easily, and solidifies to a black mass, having a conchoïdal fracture, and yielding a grey-brown powder. Before the blowpipe, it is reduced to a pale-red mass of copper-telluride. It may be fused with 1 at. cupric oxide, to a black mass having an earthy fracture. (Berzelius.)

Tellurites of Iron.—The *ferric salt* is a yellow flocculent precipitate.—The *ferrous salt* is greyish-yellow.

Tellurites of Lead.—The *neutral salt*, $Pb''TeO^3$, obtained by double decomposition with neutral acetate of lead, is a white precipitate, which when heated gives off water, turns yellow, and then melts to a translucent mass. It dissolves readily in acids, and is easily reduced before the blowpipe on charcoal to telluride of lead.—A *basic lead-salt* is produced, as a translucent bulky precipitate, on mixing tellurite of potassium with basic acetate of lead.

Tellurites of Lithium.—The *neutral salt*, $Li^2TeO^3 = Li^2O.TeO^2$, obtained by fusion, solidifies to a crystalline or tumefied mass, according to the rate of cooling.—The *ditellurite*, $Li^2O.2TeO^2$, prepared like the corresponding potassium-salt, is easily fusible, and solidifies to a crystalline mass on cooling. Cold water decomposes it into mono- and tetra-tellurite. Boiling water dissolves it, and the solution on cooling deposits the *tetratellurite*, $Li^2O.4TeO^2$, in milk-white granules. (Berzelius.)

Tellurites of Magnesium.—The *neutral salt*, $Mg''TeO^3$, obtained by precipitation, is much more soluble than the other alkaline-earthy tellurites. Its solution is decomposed by atmospheric carbonic acid into carbonate and tetratellurite of magnesium, which separates in white flocks. (Berzelius.)

Tellurite of Manganese is precipitated in white flocks having a reddish tinge.

Tellurites of Mercury.—The *mercuric salt* is a white precipitate.—The *mercurous salt* is dark-yellow, gradually turning brown, and is converted into mercuric salt on exposure to the air.

Tellurite of Nickel is a pale-green flocculent precipitate.

Tellurites of Potassium.—The *neutral* or *monotellurite*, $K^2TeO^3 = K^2O.TeO^2$, and the *ditellurite*, $K^2TeO^3.TeO^2 = K^2O.2TeO^2$, are obtained by fusing tellurous oxide with carbonate of potassium in the requisite proportions. The *monotellurite* melts at a red heat, and solidifies on cooling to a network of rather large regular crystals. It is slowly dissolved by cold, more quickly by boiling water; the solution has an alkaline taste and reaction, and is decomposed by the carbonic acid of the air.

The *ditellurite* melts, somewhat below a red heat, to yellow liquid, which solidifies on cooling to a colourless, transparent, crystalline mass. Boiling water dissolves it completely, and the solution on cooling deposits the tetratellurite as a granular precipitate.

The *tetratellurite*, or *hyperacid tellurite of potassium*, $K^2O.4TeO^2.4H^2O = 2(KHTeO^3.H^2TeO^3).H^2O$, is prepared by boiling tellurous acid for some time with carbonate of potassium, and filtering at the boiling heat. The solution, on cooling, deposits the greater part of the salt in nacreous grains, which appear under the microscope as six-sided prisms and tables. It is decomposed by cold water into mono- and di-tellurite, which dissolve, and tellurous acid, which separates as a gelatinous precipitate. The dry salt when heated gives off its water with strong intumescence, leaving the anhydrous salt, $K^2O.4TeO^2$, which melts at commencing redness, and solidifies to a colourless glass on cooling. (Berzelius.)

Tellurite of Silver, $Ag^2.TeO^3$, is a white precipitate, soluble in ammonia (Berzelius). When native telluride of silver is dissolved in nitric acid, the solution deposits, after a while, small, adamantine, acuminated, quadratic prisms, insoluble in water, and containing more than 1 at. TeO^2 to 1 at. Ag^2O. (G. Rose.)

Tellurites of Sodium.—The *neutral salt*, $Na^2TeO^3 = Na^2O.TeO^2$, obtained like the corresponding potassium-salt, forms regular crystals when slowly cooled, but swells up considerably on rapid cooling. It dissolves slowly but completely in cold water, more quickly in hot water, but does not crystallise out on cooling. Alcohol throws down from the solution a concentrated liquid, which, after a few days, yields large transparent crystals of a hydrated salt.—The *ditellurite*, $Na^2TeO^3.TeO^2 = Na^2O.2TeO^2$, obtained by fusion, like the corresponding potassium-salt, melts easily, and crystallises on cooling. It is decomposed by water, like the potassium-salt.—The *tetratellurite* or *hyperacid salt*, $Na^2O.4TeO^2.5H^2O$, or $NaHTeO^3.H^2TeO^3.H^2O$, separates from the boiling solution of the preceding salt, by slow cooling, in nacreous scales and thin six-sided tables; in other respects it resembles the hyperacid potassium-salt. (Berzelius.)

Tellurite of Strontium (neutral) is prepared like the barium-salt, which it resembles.

The *Tellurites of Thorinum, Yttrium*, and *Zirconium* are white precipitates.

Tellurite of Uranium, obtained by precipitation with a uranic salt, is a pale lemon-yellow powder.

Tellurite of Zinc is a white flocculent precipitate.

Telluric Oxide, TeO^3.—This oxide is obtained by heating the hydrate to a temperature below redness. It forms an orange-yellow mass, insoluble in water, either hot or cold, in cold hydrochloric and hot nitric acid, and in solutions of caustic alkali. When strongly heated, it gives off oxygen, and leaves tellurous oxide as a white earthy powder.

TELLURIC ACID, $H^2TeO^4 = H^2O.TeO^3$.—The potassium-salt of this acid is obtained by fusing tellurium or tellurous oxide with nitrate of potassium. The solution of this salt decomposed by a salt of barium, yields a precipitate of barium-tellurate, from which, by decomposition with sulphuric acid, telluric acid may be set free.

Telluric acid crystallises from its solution, in fine hexagonal hydrated prisms, containing $H^2TeO^4.2H^2O$, mostly forming twins. This hydrate has a metallic rather than an acid taste, and reddens litmus slightly. It dissolves slowly, but to a considerable amount in cold water, freely in boiling water. It loses its water of crystallisation at a little above 100°. The remaining acid, H^2TeO^4, is nearly insoluble in cold water, but dissolves on boiling, forming a solution from which the crystalline hydrate may be again obtained.

TELLURATES.—Telluric acid forms with the alkali-metals, neutral, acid, and hyperacid salts, represented by the formulæ, M^2TeO^4, $MHTeO^4$, and $MHTeO^4.H^2TeO^4$, respectively; also anhydrous di- and tetra-tellurites. With the other metals it forms chiefly neutral salts. The neutral and acid tellurates of alkali-metal are easily soluble in water, the anhydrous di- and tetra-tellurites sparingly soluble. Most of the other tellurates are insoluble or sparingly soluble, and are obtained by precipitation.

Most tellurates dissolve readily in cold hydrochloric acid. The solutions are not yellow, like those of the tellurites, and will bear any amount of dilution without precipitation. On boiling they give off chlorine, turn yellow, and become precipitable by water, owing to the formation of tellurous acid. The acidulated solutions of tellurates and telluric acid are decomposed, like those of the tellurites, but not very readily, by *sulphydric acid*, with precipitation of a sulphide; and by *sulphurous acid* and other reducing agents, with precipitation of tellurium, though somewhat slowly, and frequently only on the application of heat. Hence, in analysing tellurites by reduction, they should always be previously reduced to tellurites by boiling with hydrochloric acid. Tellurates when heated to redness give off oxygen, and are reduced to tellurites. Heated with charcoal and alkaline carbonate, or before the blowpipe on platinum, they behave like tellurites.

Tellurate of Aluminium is obtained by double decomposition as a white precipitate, soluble in excess of the aluminium-salt.

Tellurates of Ammonium.—The *neutral salt*, $(NH^4)^2TeO^4$, is prepared by mixing a boiling solution of the neutral potassium-salt with sal-ammoniac and a little ammonia, and separates on cooling in granular crystals, easily soluble in water, sparingly soluble in solution of ammonia or sal-ammoniac.—The *ditellurite*, $(NH^4)^2TeO^4.TeO^3 = (NH^4)^2O.2TeO^3$, is precipitated, on mixing a saturated solution of the acid sodium-salt with sal-ammoniac, as a gelatinous mass, only slightly soluble in water. When boiled with water in open vessels, it gives off ammonia; but when heated with water in sealed tubes, it partly melts to a white mass, which solidifies on cooling, and partly dissolves in the water, the solution on cooling depositing fine crystalline grains [? of the acid salt].—The *tetratellurite*, $(NH^4)^2TeO^4.3TeO^3 = (NH^4)^2O.4TeO^3$, is obtained, by decomposing the hyperacid sodium-salt with sal-ammoniac, as a white flocculent precipitate; it likewise separates from the solution of the neutral salt by evaporation at ordinary temperatures, or at a gentle heat. It dissolves with difficulty in water, and is nearly insoluble in alcohol. (Berzelius.)

Tellurates of Barium.—These salts are obtained by precipitation.—The *neutral salt*, Ba separates as a bulky precipitate, which soon sinks down, and forms a white powder when dry. It gives off water at 200°, dissolves sparingly in cold, more easily in boiling water.—The *acid salt*, $Ba''H^2(TeO^4)^2.2H^2O$, is a bulky flocculent mass, more soluble in water than the neutral salt.—The *anhydrous tetratellurate*, $Ba''O.4TeO^2$, is a bulky mass, more soluble in water than either of the preceding [is it really anhydrous?]. It turns yellow when heated, but becomes white again on cooling. (Berzelius.)

Tellurate of Cadmium, $Cd''TeO^4$, is obtained, as an amorphous white precipitate, on mixing the neutral solutions of cadmium-nitrate and a tellurate of alkali-metal. (Oppenheim.)

Tellurates of Calcium, $Ca''TeO^4$, is precipitated in white non-coherent flocks, soluble in hot water. (Berzelius.)

Tellurate of Chromium forms grey-green flocks, reddish by transmitted light; it dissolves in excess of the chromic salt, by which it is precipitated.

Tellurate of Cobalt is precipitated in bluish-red bulky flakes.

Tellurates of Copper.—The *neutral salt* is a celandine-green precipitate; the *acid salt* is somewhat lighter.

Tellurates of Iron.—The *ferric salt* separates as a pale-yellow flocculent precipitate, soluble in excess of the precipitating ferric salt.—The *ferrous salt* is a white precipitate, quickly changing colour in the air like other ferrous salts.

Tellurates of Lead.—Obtained by precipitation.—The *neutral salt*, $Pb''TeO^4 = Pb''O.TeO^3$, is a white precipitate, somewhat soluble in water.—The *ditellurate*, $Pb''O.2TeO^3$, is somewhat more soluble.—The *tetratellurate*, $Pb''O.4TeO^3$, turns yellow when heated, but becomes white again on cooling: it is moderately soluble in water.—A *basic lead-salt* separates, as a white bulky precipitate insoluble in water, on mixing the solution of a neutral tellurate of alkali-metal with basic acetate of lead (Berzelius).—A *nitrato-tellurate of lead* is formed (according to Oppenheim) on mixing a solution of lead-nitrate with free telluric acid; it is a white powder.

Tellurates of Lithium.—Prepared like the corresponding potassium-salts. The *neutral* and *acid salts* dry up to gummy masses.—The *hyperacid salt* is also a gummy mass, which is converted at 100° into a white insoluble powder; at a still higher temperature, it gives off water and turns yellow. (Berzelius.)

Tellurates of Magnesium.—These salts, being much more soluble in water than the tellurates of the other alkaline earth-metals, must be precipitated from very concentrated solutions.—The *neutral* and *acid salts* are white flocculent precipitates. (Berzelius.)

Tellurate of Manganese separates in white flocks, having a faint reddish tinge.

Tellurates of Mercury.—The *mercuric salt* is precipitated in bulky white flocks.—The *mercurous salt* is a dark yellowish-brown precipitate.—A *mercurous nitrato-tellurate* is produced (according to Oppenheim) by adding free telluric acid to a concentrated solution of mercurous nitrate. It forms at first a white curdy precipitate, but acquires a faint yellow colour on exposure to the air.

Tellurate of Nickel is precipitated in pale-greenish flocks.

Tellurates of Potassium.—These salts are prepared by dissolving the required quantities of telluric acid and potassium-carbonate in hot water.—The *neutral salt*, $K^2TeO^4.5H^2O$, may also be prepared by supersaturating crystallised telluric acid, or its concentrated aqueous solution, with caustic potash. It is very slightly soluble in water containing potash, and separates therefrom as a soft gummy coagulum. It dissolves on warming the liquid, and separates by slow cooling in needle-shaped crystals, which when heated give off water, and cake together in a white mass. According to Handl (Jahresb. 1861, p 266), it forms rhombic crystals of prismatic character, isomorphous with those of neutral potassium-sulphate, and exhibiting the combination $\infty\breve{P}2 . P . \infty\breve{P}\infty . \infty\breve{P}\infty$. Angle $\infty\breve{P}2 : \infty\breve{P}2 = 69° 11'$; $P : \infty\breve{P}\infty = 123° 42'$; $P : P$ (in the terminal edges) $= 122° 36'$ and $132° 16'$. When exposed to the air, they become moist, without deliquescing, and are converted into a mixture of acid tellurate and carbonate of potassium. On mixing the solution of the salt with a stronger acid, it deposits acid or hyperacid tellurate of potassium, according to the quantity of acid added (Berzelius).—The *acid salt*, $2KHTeO^4.3H^2O$, is sparingly soluble in cold, much more soluble in hot water, and separates from the hot solution by slow cooling, in fine woolly crystallisations. On evaporating the aqueous solution over a water-bath, it remains as a white saline mass, gummy on the edges. It has an alkaline reaction, and a metallic, somewhat alkaline taste. When heated, it gives off its water, and turns yellow even far below redness. Water decomposes the yellow mass, dissolving neutral tellurate of potassium, and leaving yellow tetratellurate (Berzelius).—The *hyperacid salt*, $2(KHTeO^4.H^2TeO^4).H^2O$, is a loose white powder, somewhat soluble in water. It gives off the greater part of its water at a gentle heat, retaining however a small quantity till it turns yellow; at a higher temperature, it is reduced to tellurite. By repeated crystallisation from its aqueous solution, it is partially decomposed, the crystals becoming mixed with those of the acid salt, while free telluric acid remains in the mother-liquor (Berzelius).—The *anhydrous tetratellurate*, $K^2O.4TeO^3$, may be obtained by heating the acid tellurate to a temperature below redness, whereupon it breaks up into water, which is evolved; neutral tellurate of potassium, which may be dissolved out; and the anhydrous tetratellurate, which remains undissolved as a yellow mass, insoluble in hydrochloric acid and in nitric acid, except after prolonged boiling. Its formation is represented by the equation:

$$6KHTeO^4 = 2K^2TO^4 + K^2TeO^4.3TeO^3 + 3H^2O.$$

Tellurates of Silver.—Telluric acid forms a neutral salt, two acid salts, and two basic salts of silver. The neutral and acid salts are obtained by double decomposition with concentrated solutions of silver-nitrate and neutral tellurate of alkali-metal.—The *neutral salt*, Ag^2TeO^4, is a dark-yellow powder, which is resolved by water, especially at the boiling heat, into a soluble acid and an insoluble basic salt. Its ammoniacal solution is colourless.—A *nitrato-tellurate of silver* separates, immediately on adding telluric acid to a concentrated solution of silver-nitrate, as a colourless crystalline precipitate, which turns slightly yellow in contact with the air, and brown when moistened with ammonia. Hydrochloric acid decomposes it, with separation of silver-chloride (Oppenheim).—The *ditellurate* and *tetratellurate of silver* are reddish-yellow flocculent precipitates.

The *tribasic salt*, $3Ag^2O.TeO^3 = 2Ag^2O.Ag^2TeO^4$, is produced on mixing the ammoniacal solutions of the neutral salt and silver-nitrate, and remains on evaporation as a black-brown saline mass.—The same compound separates as a reddish-yellow precipitate, quickly turning brown, on mixing a very dilute solution of silver-nitrate with acid tellurate of potassium.—The *sesquibasic salt*, $3Ag^2O.2TeO^3$, remains as an anhydrous liver-coloured powder, on boiling the neutral salt with water. (Berzelius.)

Tellurates of Sodium.—These salts resemble the corresponding potassium-salts, and are prepared in like manner.

Tellurate of Strontium is prepared like the calcium-salt, which it resembles.

Tellurate of Thorinum is a white pulverulent precipitate, insoluble in excess of the thorinum-salt.

Uranic tellurate is a pale-yellow powder.

Tellurates of Yttrium.—The *neutral tellurates* and *ditellurates* are obtained by precipitating the neutral and acid tellurates of potassium with an yttrium-salt.

Tellurate of Zirconium, obtained by double decomposition, is a white powder.

TELLURIUM, SELENIDE OF. Tellurium and selenium may be fused together in all proportions, the combination being attended with evolution of heat. The product is an iron-grey brittle mass, which has a crystalline fracture, melts below a red heat, boils at a higher temperature, and may be volatilised without decomposition if excluded from the air. When heated in contact with the air, it yields colourless drops, possibly consisting of a selenate of tellurium. (Berzelius.)

TELLURIUM, SULPHIDES OF. Tellurium forms two sulphides corresponding to the oxides.

Tellurous Sulphide, TeS^2, is formed by the action of sulphydric acid on a tellurous salt, or on the acidified solution of a tellurite (p. 711); also by exposing the solution of a sulphotellurite of alkali-metal to the air. It is a dark-brown or black substance, which softens at a moderate heat, and acquires a semi-metallic lustre on cooling. When strongly heated it evolves sulphur.

Tellurous sulphide combines with the sulphides of basylous metals, forming the sulphotellurites, all of which appear to contain 3 at. basylous sulphide to 1 at. tellurous sulphide, being represented by the general formula $3M^2S.TeS^2 = 2M^2S.M^2TeS^3$.

The sulphotellurites of the *alkali-metals* and of *magnesium* are most readily prepared by saturating the aqueous solutions of the corresponding tellurites with sulphydric acid gas. The solid anhydrous sulphotellurites of alkali-metal have a brownish-yellow colour; those which contain water of crystallisation are pale-yellow; they dissolve easily and with pale-yellow colour in water; less easily in alcohol, with separation of tellurous sulphide. Acids added to the solutions throw down tellurous sulphide. In the dry state these salts may be ignited in close vessels without decomposition, and at ordinary temperatures they remain unaltered for a considerable time in contact with the air; but their solutions decompose quickly in contact with the air, with formation of alkaline hyposulphite, and separation of tellurous sulphide.—The *ammonium-salt*, $3(NH^4)^2S.TeS^2$, crystallises by evaporation in a vacuum over potash, in pale-yellow four-sided prisms, which give off sulphide of ammonium in contact with the air.—The *potassium-salt*, $3K^2S.TeS^2$, separates by evaporation in a vacuum, in pale-yellow prisms, easily melting to a black liquid, which solidifies to a brown-yellow mass still soluble in water. In contact with the air, the salt decomposes and turns black.—The *sodium-salt* forms an amorphous pale-yellow mass, which decomposes quickly in contact with the air.—The *lithium-salt* exhibits similar characters.—The *magnesium-salt*, which may be prepared as above, or by precipitating the barium-salt with magnesium-sulphate, and evaporating the filtrate in a vacuum, forms a pale-yellow crystalline mass, soluble in water and in alcohol.

The sulphotellurites of the *alkaline earth-metals* are prepared by boiling the corresponding metallic sulphides with tellurous sulphide and water.—The *barium-salt* separates, on evaporating the filtrate in a vacuum, in large, transparent, pale-yellow, obliquely truncated, four-sided prisms. It is tolerably permanent in the air, and dissolves very slowly in water.—The *strontium-salt* forms a pale-yellow mass, tolerably permanent in the air, and soluble in water.—The *calcium-salt* is a yellow amorphous mass, somewhat soluble in water.

The sulphotellurites of the *heavy metals* are insoluble in water, and are obtained by precipitation.—The *cadmium-* and *cerium-salts* are brown-yellow precipitates, which gradually become darker in colour.—The *ferric salt* forms dark-brown, easily fusible flocks; the *ferrous salt* is a black precipitate.—The *gold-salt* (auric), $AuS^3.TeS^2$, is deposited, after some days, in black flocks, from a mixture of auric chloride and potassium-sulphotellurite.—The *lead-salt* is a brown precipitate, which turns black on drying.—The *mercurous salt*, $3Hg^2S.TeS^2$, is a dark-brown precipitate, which when heated gives off mercury, and is converted into a yellow-brown mass of the *mercuric salt*, $3HgS.TeS^2$.—The *platinic salt*, $3PtS^2.2TeS^2$, separates after some days, from a mixture of platinic chloride and potassium-sulphotellurite, in translucent dark-blue flocks, which appear black when dry.—The *silver-salt*, $3Ag^2S.TeS^2$, is a bulky black precipitate, which when dry acquires metallic lustre by trituration.—The *zinc-salt*, $3ZnS.TeS^2$, is a light-yellow precipitate which gradually turns brown.

Telluric Sulphide, TeS^3.—This compound is produced by saturating a solution of telluric acid with sulphydric acid gas, and gradually separates on leaving the liquid to itself in a closed vessel placed in a warm situation, covering the sides of the vessel with a blackish-grey, metallically lustrous coating, which may be rubbed off in spangles. It unites with basylous metallic sulphides, forming the sulphotellurates, which, however, have been but little investigated. (Berzelius.)

Sulphotellurate of Potassium is obtained by saturating a solution of potassium-tellurate with sulphydric acid gas. After the liquid has been filtered from the resulting black precipitate of telluric sulphide, which does not redissolve on adding potash and again passing sulphydric acid gas into the liquid, the filtrate may be concentrated by boiling without decomposition. The liquid then acquires a red colour, and deposits sulphotellurate of potassium as a light-yellow granulo-crystalline mass. (Oppenheim, J. pr. Chem. lxxi. 279.)

Sulphotellurate of Sodium is prepared like the potassium-salt. On adding soda-ley after the precipitate of telluric sulphide has settled down, and again passing sulphydric acid gas into the liquid, the precipitate quickly redissolves; and on evaporating the solution nearly to dryness, the sulphotellurate of sodium separates, in needle-shaped crystals of a sulphur-yellow colour. (Oppenheim.)

TELLUROMETHYL. See METHYL, TELLURIDE OF, iii. 992.

TELLUROUS SALTS. Salts formed by dissolving tellurous hydrate in acids (p. 713).

TEMPERATURE. See HEAT (iii. 18).

TEMPERING. The softening of steel, cast-iron, and other metals by ignition and slow cooling.

TEMPLIN-OIL. *Oil of Pine-cones. Tannenzapfenöl.*—An oil isomeric with, and very similar to, oil of turpentine, obtained by distillation of the cones of *Pinus Pumilio*, Hnk. (*P. Mughus*, Scop.), and in some parts of Switzerland from the cones of the silver-fir (*Abies Picea*, *Pinus Picea* L. *Abies pectinata*, Dec.). When recently prepared by distillation with water, it is colourless, but becomes greenish-yellow on exposure to the air. It has a balsamic odour, like that of lemon-oil; a specific gravity of 0·862 at 12°; begins to boil at 155°; but the greater part distils over between 173° and 177°, the boiling-point ultimately rising to 200°. By repeated rectification a camphene, $C^{10}H^{16}$, is obtained, having a specific gravity of 0·856 at 6°, and boiling constantly at 172°. (Flückiger, Jahresb. 1856, p. 642.)

Templin-oil agrees with oil of turpentine in solubility and refracting power. I column 100 millimetres long, it turns the plane of polarisation 85° to the left for the transition-tint, and 66° for the red ray: the oil obtained from it by rectification below 173° turns the plane of polarisation 92° to the left for the transition-tint. (Berthelot, J. Pharm. [3], xxix. 38.)

Templin-oil resinises quickly on exposure to the air, and turns acid, with formation of ozone. When mixed with ¼ vol. nitric acid and ⅛ vol. alcohol, it forms terpin or hydrate of turpentine, more quickly on addition of 1¼ vol. water. It absorbs hydrochloric acid gas, but without forming a crystallisable camphor. When the oil, saturated with hydrochloric acid gas, is treated with fuming nitric acid, a crystalline compound, $C^{10}H^{16}.HCl$, is formed, having a rotatory power of $-23°$. When templin-oil is mixed with one-third of its weight of absolute alcohol, and then saturated with hydrochloric acid gas, the liquid solidifies to a magma of the camphoroïdal compound, $C^{10}H^{16}.2HCl$, insoluble in water and in cold alcohol, but easily soluble in hot alcohol, from which solution it crystallises in laminæ. It dissolves in volatile and fixed oils in nitric acid and in sulphuric acid, melts at 55°, and solidifies to a radio-crystalline mass on cooling, but is not volatile without decomposition.

The oil obtained from the young branches and needles of *Pinus Pumilio* (iv. 649) is probably identical with templin-oil.

TENNANTITE. An arsenical fahl-ore from the Cornish mines, particularly near Redruth and St. Day, occurring in well-defined, monometric, tetrahedral crystals, isomorphous with tetrahedrite, and exhibiting imperfect dodecahedral cleavage. Hardness = 3·5 to 4. Specific gravity = 4·4 to 4·9. Lustre metallic. Colour, blackish lead-grey to iron-black; streak, dark reddish-grey. Fracture uneven. Before the blowpipe it emits copious arsenical fumes, and finally melts to a black scoria, which acts upon the magnet.

Analyses: *a* by Wackernagel; *b* by Rammelsberg (*Mineralchemie*, p. 88):

	S.	As.	Cu.	Fe.		
a.	26·88	20·53	48·68	3·09	=	99·18
b.	26·61	19·03	51·62	1·95	=	99·21

These analyses may be represented by the formula $(Cu^2; Fe'')S.2As^2S^3$, different from that of arsenical tetrahedrite—namely, $4M''S.As^2S^3$.

TENORITE. Native cupric oxide, occurring, according to Semmola (Bull. géol. xiii. 206), in the cracks and pores of Vesuvian lava, above Torre del Greco, forming very thin hexagonal plates, scales, and earthy particles, having a dark steel-grey colour, and metallic to dull lustre. Thin laminæ exhibit a brown translucence.

TEPHROITE. Orthosilicate of manganese, $Mn''SiO^4$, from Sparta, New Jersey. (See SILICATES, p. 254.)

TEPHROSIA. The leaves of *Tephrosia apollinea* (Dec.), a leguminous plant indigenous in Upper Egypt, are very much like those of *Cassia obtusa*, and are said to occur in commerce as *Folia sennæ halipensia*. (Nees v. Esenbeck, J. Pharm. [3], vi. 185.)

TERACRYLIC ACID. Syn. with PYROTEREBIC ACID (iv. 776).

TERATOLITE. Ferruginous lithomarge, from the coal-beds near Zwickau, in Saxony.

TERATONATRITE. Syn. with Glauber's salt.

TERBIUM and **ERBIUM.** Metals supposed to exist, together with yttrium, in the gadolinite of Ytterby, in Sweden. Mosander in 1843 (Ann. Ch. Pharm. xlviii. 220) examined the crude yttria obtained from gadolinite, by the process of Berzelius (see YTTRIUM), and concluded that it was a mixture of three earths of different basic power. The most basic of these—which was first precipitated from solution of the earth in hydrochloric acid by ammonia—he designated as erbia, the next as terbia, retaining the name of yttria for the least basic. A more complete separation is effected by fractional precipitation with an acid oxalate. For this purpose, the crude yttria is dissolved in excess of hydrochloric acid, and the liquid is added by drops to a solution of acid potassium-oxalate, as long as the resulting precipitate redissolves on agitation. The crystalline precipitate, chiefly consisting of erbium-oxalate, which then separates after some hours, is collected on a filter; and the filtrate is gradually mixed with more potassium-oxalate, which throws down a fresh precipitate containing a larger proportion of terbium, while the last precipitates contain scarcely anything but yttrium. The first precipitates are almost always reddish; the last are colourless. On the other hand, when a mixture of the oxalates of erbium, terbium, and yttrium is digested with dilute sulphuric acid, the yttrium-salt is chiefly dissolved at first, then the terbium, and lastly the erbium-salt. (Mosander).

The metals erbium and terbium have not been isolated. The characters of erbium-oxide or erbia, and of one or two erbium-salts, as determined by Mosander, have been already described (ii. 497); erbia is especially distinguished by being yellow after ignition in the air, and becoming colourless by ignition in hydrogen.

The characters of terbium-oxide or terbia are not described by Mosander; but its salts are described as having a saccharine and astringent taste. In the solid state, they exhibit an amethyst-colour, but not of constant tint or intensity.—The *nitrate* is a rose-red, crystalline, deliquescent mass, and its solution becomes coloured during evaporation, even before any separation of crystals takes place.—The *sulphate* forms crystals, which are larger than those of yttrium-sulphate, and effloresce at about 50°, crumbling to a white powder. (Mosander.)

Subsequent investigations by different chemists have, however, thrown considerable doubt on the existence of terbium. Berlin in 1860,[*] in applying the preceding method of separation on a larger scale, obtained only erbia and yttria, the intermediate precipitates being always resolvable, by repeated fractional precipitation, into the oxalates of erbium and yttrium. He was also unable to obtain the sulphate efflorescing at 50°, which Mosander describes as distinguishing terbium from erbium.

Similar results have been obtained by Popp (Ann. Ch. Pharm. cxxxi. 179), who moreover finds that the absorption-spectrum of an erbium-solution exhibits certain bands, identical with those of didymium (ii. 322); and that on passing chlorine through the solution of an erbium-salt mixed with sodium-acetate, and heated to the boiling-point, the peculiar yellow precipitate characteristic of cerium (i. 831) is obtained. Hence Popp concludes that the supposed earths, erbia and terbia, are nothing but yttria contaminated with the oxides of the cerium-metals. His experiments cannot, however, be considered as disproving the existence of erbium, inasmuch as mixtures of erbium-salts with those of cerium and didymium might exhibit the characters above mentioned; but Popp's results agree with those of Berlin, in tending to show that Mosander's terbia is really a mixture of erbia and yttria; and this conclusion is further corroborated by the recent experiments of Bahr and Bunsen (Ann. Ch. Pharm. cxxxvii. 1). These chemists separate erbia and yttria as follows.

The precipitate formed by oxalic acid, in the solution obtained by heating gadolinite with hydrochloric acid, contains the oxalates of erbium and yttrium, besides those of calcium, cerium, lanthanum, and didymium, with traces of manganous oxalate and silica. These oxalates are converted into nitrates; the solution is treated with sulphate of potassium, with the usual precautions (i. 831), to separate the cerium-metals; the erbium and yttrium, which still remain in solution, are again precipitated by oxalic acid; the oxalates are ignited; and the residual oxides, after being carefully freed from admixed potassium-carbonate by boiling with water, are dissolved in nitric acid, and again precipitated from the acid solution by oxalic acid, this series of operations being repeated till the solution of the mixed earths in nitric acid, when examined in the spectral apparatus, no longer exhibits the absorption-bands characteristic of didymium. The last portions of calcium and magnesium are separated by precipitating the acid solution of the mixed earths with ammonia, the calcium and magnesium then remaining in solution; the precipitate is dissolved in nitric acid; and the solution, now containing nothing but erbia and yttria, is precipitated by oxalic acid.

To separate the erbia and yttria, the oxalates are converted into nitrates; the solution is evaporated in a platinum-dish, till the first bubbles of nitrous acid make their appearance; and the dish is quickly cooled by placing it in cold water, whereupon the viscid mass solidifies to an extremely brittle glass. On dissolving the mass in a quantity of warm water just sufficient to prevent the solution from becoming turbid on boiling, nitrate of erbium, still containing yttrium, separates on slow cooling in needles, which must be separated from the mother-liquor by decantation, and quickly rinsed with water containing about 3 per cent. of nitric acid. This mother-liquor, treated in a similar manner, yields a second crop of crystals of erbium-nitrate containing yttrium; the mother-liquor of these yields a third crop, and so on, the proportion of yttrium-nitrate in the successive crops of crystals continually increasing. By mixing a certain number of the earlier and comparatively pure crops of crystals, and treating them in a similar manner, products are obtained of still greater purity; and by repeating this mode of treatment several times, nitrate of erbium is ultimately obtained containing no appreciable quantity of yttrium.

Pure erbia, obtained by ignition of the nitrate or oxalate, has a faint rose-red colour (not yellow, as stated by Mosander). It does not melt at the strongest white heat, but aggregates to a spongy mass, glowing with an intense *green* light, which, when examined by the spectroscope, exhibits a *continuous* spectrum intersected by a number of bright bands. Solutions of erbium-salts, on the other hand, give an absorption-spectrum exhibiting dark bands, and *the points of maximum intensity of the light bands in the emission-spectrum of glowing erbia coincide exactly in position with the points of greatest darkness in the absorption-spectrum.* The position of these bands is totally different from those in the emission- and absorption-spectra of didymium; in fact, there is not a single line of the erbium-spectrum which corresponds with that of didymium. (Bahr and Bunsen.)*

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[*] Forhandlinger ved de Skandinaviske Naturforskeres attende Möde i Kjöbenhaven, 1860, p. 448.

Erbia is a protoxide, $Eb''O$, containing 87·6 per cent. erbium and 12·4 oxygen; it does not unite directly with water. It dissolves slowly but completely in warm hydrochloric, nitric, and sulphuric acids. The erbium-salts have a rose-red colour, deeper in the hydrated than in the anhydrous state; they have an acid reaction and sweet astringent taste.—*Nitrate of Erbium*, obtained as above described, is a basic salt, $Eb''(NO^3)^2.Eb''O.3H^2O$, crystallising in small imperfectly-defined needles, having a light rose-colour, permanent in the air, giving off their crystallisation-water at a moderate heat, and being converted into erbia at a red heat without change of form. It dissolves with difficulty in nitric acid, and is decomposed by water into nitric acid and a gelatinous hyperbasic salt.—The *sulphate*, $3Eb''SO^4.8H^2O$, isomorphous with the sulphates of yttrium and didymium, forms light rose-coloured crystals, which give off their water of crystallisation when heated, and recover it with great rise of temperature when moistened with water. The hydrated salt dissolves very slowly in water, the anhydrous salt very quickly, a character exhibited also by the sulphates of the cerium-metals. It is partially decomposed by ignition.—The *oxalate*, $C^2Eb''O^4.H^2O$, is precipitated from boiling acid solutions of erbium-salts as a light rose-coloured, heavy, sandy powder, which may be easily washed by decantation, and does not give off its water till heated nearly to the temperature at which it decomposes.

The mother-liquors from the several crystallisations of erbium-nitrate contain nitrate of yttrium, together with a certain quantity of the erbium-salt and the nitrates of the cerium-metals, which have not gone down with the nitrate of erbium in the successive crystallisations, but have accumulated in the mother-liquors. To obtain a pure yttrium-salt, therefore, the cerium-metals must, in the first place, be removed by repeated treatment with sulphate of potassium, till the remaining solution, when examined by the spectroscope, shows no trace of the didymium-lines. The sulphate of yttrium thus far purified, but still containing erbium, is next reconverted into nitrate; the solution of this salt is evaporated; the residue heated nearly to redness; and the resulting mixture of the oxides and hyperbasic nitrates of yttrium and erbium is treated with cold water, whereby a solution is obtained, containing nitrate of yttrium with less erbium-salt than before, and a residue rich in erbium; and by repeating this treatment several times, a nitrate of yttrium is at length obtained, which exhibits no trace of an absorption-spectrum, and when ignited leaves pure colourless yttria. (See YTTRIUM.)

The result of the whole series of operations is, therefore, to separate the crude yttria obtained from gadolinite into two earths, yttria and erbia, without any indication of an earth (the so-called terbia) of intermediate basicity.

On the other hand, Delafontaine (Ann. Ch. Pharm. cxxxiv. 99; Jahresb. 1864, p. 196; Bull. Soc. Chim. [1866] i. 168) still maintains the separate existence of erbia and terbia. He finds that the first precipitates thrown down by acid potassic oxalate (as in Mosander's method), from a solution of crude yttria, yield, on ignition, a yellow residue; and if this be redissolved, and subjected several times to the same treatment, an earth is obtained of continually deeper yellow colour, and consisting mainly of erbia, with comparatively small quantities of terbia and yttria; from which it may be further purified by dissolving it in nitric acid, evaporating to dryness, redissolving in water, saturating the neutral solution in the cold with pulverised potassic sulphate, and washing the resulting precipitate (consisting of erbio-potassic sulphate) with a saturated solution of potassic sulphate, which dissolves the double sulphates of the other two metals. The erbio-potassic salt dissolves easily in hot water, and the solution, treated with potash, yields erbium-hydrate, which may be redissolved, and completely purified from terbium and yttrium by repetition of the same treatment.

Anhydrous erbia, thus obtained, has a yellow colour of various depths, but becomes white by ignition in hydrogen. The hydrate is white, absorbs carbonic acid from the air, and when heated to redness, leaves the anhydrous oxide in dense hard lumps of a deep orange-yellow colour. Its solutions are colourless, or sometimes have a faint rose-colour, and do not exhibit any absorption-spectrum.

Terbia, the separation of which from yttria is not specially described, is (according to Delafontaine) an earth of a pale rose-colour, and does not become colourless by ignition in hydrogen. It dissolves easily in acids, forming rose-coloured solutions, which yield an absorption-spectrum. Delafontaine is of opinion that the earth described by Bahr and Bunsen as erbia, is really terbia, the true erbia, which is first precipitated by oxalic acid from the solution of the mixed earths, having, as above mentioned, a yellow (not a rose) colour, and not producing an absorption-spectrum. Bahr and Bunsen, on the contrary, are of opinion that the yellow colour and other peculiarities of Delafontaine's erbia are to be attributed to imperfect separation of the cerium-metals.

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* The paper above referred to is accompanied by exact diagrams of the erbium- and didymium-spectra.

Further experiments are perhaps required, to afford a perfectly satisfactory answer to the question whether crude yttria is a mixture of three earths or of only two; but, for the present, the very carefully conducted experiments of Bahr and Bunsen must be regarded as throwing great doubt on the existence of the third of these earths—the so-called terbia. The fact which tells most strongly in favour of the opposite view, is that Delafontaine's terbia exhibits an absorption-spectrum, whereas his erbia does not; but the descriptions hitherto given of his methods of separation are not sufficiently precise to enable us to judge of their efficiency.

According to Delafontaine, the atomic weight of yttrium is 74·4 (yttria = $Y''O$); that of erbium is higher, and that of terbium higher still. He further regards it as probable that gadolinite contains a fourth metal, whose salts have an absorption-spectrum partly corresponding with that of didymium.

According to Bahr and Bunsen, the atomic weight of yttrium is 61·7, and that of erbium 112·6.

TEREBAMIC ACID. $C^7H^{11}NO^3 = \left.\begin{matrix}H^2\\(C^7H^8O^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. *Terebamide.*—This compound is produced, by heating terebic acid in ammonia-gas to 140°–160°, as a sublimate, which dissolves slightly in cold, easily in hot water and alcohol. The solutions are neutral to litmus, and do not decompose carbonates. Terebamic acid dissolves easily in caustic alkalis, and is separated from the solution by acids in its original state. —The *barium-salt*, $C^{14}H^{20}Ba''N^2O^6.2H^2O$, is easily soluble in water, and dries up on evaporation to a gum: it is precipitated in the crystalline state by alcohol, and forms, after drying, a loose web of microscopic needles having a silky lustre. (Handw. d. Chem. viii. 575.)

TEREBAMIDE. See the preceding article.

TEREBENE. An optically inactive isomer of turpentine-oil (*q. v.*).

TEREBENES. Syn. with CAMPHENES (i. 724).

TEREBENIC ACID. Syn. with TEREBIC ACID.

TEREBENTHENE. One of the isomers of turpentine-oil obtained by the decomposition of the hydrochlorate, $C^{10}H^{16}.HCl$, or the hydrobromate, $C^{10}H^{16}.HBr$. It also forms the chief portion of the turpentine of *Pinus maritima*. (See TURPENTINE OIL.)

TEREBENTILIC ACID. $C^8H^{10}O^2$. (J. Personne, Ann. Ch. Pharm. c. 253.)—This acid is obtained by passing the vapour of fused turpentine-hydrate over soda-lime heated to 400°, and treating the resulting mass with hydrochloric acid; the reaction is attended with the evolution of large quantities of marsh-gas and hydrogen:

$$C^{10}H^{20}O^2 = C^8H^{10}O^2 + 2CH^4 + H^2.$$

This acid is white, has a faint odour resembling that of the goat, is heavier than water, melts at 90°, and distils with partial decomposition at 250°. It is insoluble in cold, but soluble in boiling water, and separates, on cooling, as a powder consisting of small needle-shaped crystals; it is very soluble in alcohol and in ether. By sublimation, it crystallises in small spangles, apparently having the form of oblique prisms. Its vapour is acrid, and attacks the nose strongly.

Terebentilic acid is monobasic.—Its *calcium-salt*, formed by treating the acid with lime, crystallises in small silky needles, resembling sulphate of quinine.—The *lead-salt* is uncrystallisable, and resembles gum-arabic.—The *silver-salt*, $C^8H^9AgO^2$, is slightly soluble in boiling water, and crystallises on cooling.

With alcohol, terebentilic acid easily forms an ether having the odour of pears and pine-apples.

TEREBENZIC ACID. An acid produced, according to Cailliot (Ann. Ch. Phys. [3], xxi. 31), together with terephthalic acid, by the action of nitric acid on turpentine-oil. It is separated from the terephthalic acid by boiling water or cold alcohol, and crystallises from the aqueous solution, on cooling, in small shining needles said to have the composition $C^{14}H^7O^4$. It volatilises easily with the vapour of boiling water, melts at 169°, boils at a much higher temperature, but sublimes at 100° when heated in open vessels. Its ether has an agreeable odour of anise, and boils at 130°. The metallic terebenzates are about as soluble in water as the benzoates.

TEREBIC ACID. $C^7H^{10}O^4 = \left.\begin{matrix}(C^7H^8O^2)''\\H^2\end{matrix}\right\}O^2$.—A product of the action of nitric acid upon turpentine-oil, discovered by **Bromeis** (Ann. Ch. Pharm. xxxvii. 297), who called it *turpentinic acid*; further examined by **Rabourdin** (J. Pharm. [3], vi. 185), who designated it as *terebilic* or *terebenic acid*; by **Cailliot** (L. Institut. 1849, p. 353), and lastly by **Svanberg** and **Eckmann** (J. pr. Chem. lxvi. 220).

To prepare it, oil of turpentine is heated with four or five times its weight of nitric acid diluted with an equal bulk of water, as long as red fumes are evolved, whereby a reddish-yellow brittle resin and a yellow acid liquid are obtained. This liquid, evaporated to a syrup, and diluted with a large quantity of water, deposits a whitish-yellow precipitate, having the consistence of pitch; and the watery liquid separated therefrom yields crystalline terebic acid. (**Svanberg** and **Eckmann**.)

Terebic acid crystallises (according to **Bromeis**) in tolerably regular forms, appearing under the microscope as four-sided prisms with oblique terminal faces, and exhibiting an extraordinary lustre on their lateral faces. It has a purely acid taste, dissolves slightly in cold, more readily in boiling water, easily in alcohol and ether. It is not decomposed by nitric acid at the boiling heat, but sulphuric acid chars it. The acid melts at 200° without loss of weight; but at a higher temperature it begins to boil, and is resolved into carbonic anhydride and pyroterebic acid: $C^7H^{10}O^4 = CO^2 + C^6H^{10}O^2$.

Terebates.—Terebic acid is dibasic. It decomposes carbonates, forming acid salts, $C^7H^9MO^4$ and $C^{14}H^{18}M''O^8$, which have an acid reaction, but do not exert any further action upon carbonates. In contact with metallic oxides and hydrates, however, the acid forms neutral salts, $C^7H^8M^2O^4$ and $C^7H^8M''O^4$. It resembles salicylic acid in forming acid more readily than neutral salts. It also forms acid ethers, which act with bases like a monobasic acid.

The neutral terebates all contain water of crystallisation, and retain at least one atom of it until heated to a temperature at which they decompose. When dehydrated as far as possible without decomposition, they have the composition $C^7H^8M''O^4.H^2O$. Hence they are regarded by Cailliot as salts of a peculiar acid, $C^7H^{12}O^5$, which he calls **diaterebic acid**. But, as they yield terebic acid when decomposed by acids, this supposition does not appear to rest on very good grounds.

Terebates of Ammonium.—The *neutral salt* is deliquescent and uncrystallisable. —The *acid salt*, $C^7H^9(NH^4)O^4$, forms very soluble prisms; which give off their ammonia, slowly at ordinary temperatures, quickly at 100°.

Terebates of Barium.—The *neutral salt*, $2C^7H^8Ba''O^4.5H^2O$, obtained by adding baryta-water to a solution of the acid salt, and precipitating the excess of baryta with carbonic acid, dries up to a gummy mass, which gives off 2 at. water at 140°, leaving the salt $2C^7H^8Ba''O^4.3H^2O$. This hydrate, which appears also to be precipitated by alcohol from the aqueous solution, deliquesces on exposure to the air, and then yields crystals of another hydrate, $C^7H^8Ba''O^4.3H^2O$ (**Cailliot**).—The *acid barium-salt*, $C^{14}H^{18}Ba''O^8.2H^2O$, or $C^7H^8Ca''O^4.C^7H^{10}O^4.2H^2O$, obtained by treating the aqueous acid with carbonate of barium, is precipitated from its syrupy solution by alcohol in needles (**Cailliot**); according to **Svanberg** and **Eckmann**, it is uncrystallisable. A more dilute solution mixed with alcohol slowly deposits nodules of the neutral salt, while free terebic acid remains in solution.

The *neutral calcium-salt* separates, by spontaneous evaporation of its solution, in microscopic tables, containing $2C^7H^8Ca''O^4.5H^2O$; but on boiling the solution, it is deposited in small crystals containing $C^7H^8Ca''O^4.H^2O$.

Terebates of Lead.—The *neutral salt*, $3C^7H^8Pb''O^4.2H^2O$, forms crystalline nodules, which are insoluble in cold water, and are decomposed by boiling water, with formation of a basic salt.—A *basic lead-salt*, $2C^7H^8Pb''O^4.Pb''H^2O^2.3H^2O$, is also precipitated on evaporating a solution of 1 at. lead-oxide in 1 at. terebic acid.—**Cailliot** likewise describes a salt containing $2C^7H^8Pb''O^4.5H^2O$, which he calls *metaterebate of lead*, representing it as $2PbO.C^{14}H^{18}O^{11}$.—The *acid lead-salt*, $C^{14}H^{18}Pb''O^8.H^2O = C^7H^8Pb''O^4.C^7H^{10}O^4.H^2O$, is obtained by saturating the aqueous acid with litharge, taking care that the latter is not added in excess, and crystallises from the liquid, evaporated to a syrup, in small white groups of crystals resembling cauliflower-heads.

The *acid potassium-salt*, $2C^7H^9KO^4.H^2O$, obtained by dissolving carbonate of potassium in an equivalent quantity of the acid, and evaporating to a syrup, forms very soluble crystals, which give off their water at 100°.—The *acid sodium-salt*, $2C^7H^9NaO^4.H^2O$, prepared like the preceding, also gives off its water at 100°.

Silver-salts.—The *neutral salt*, $C^7H^8Ag^2O^4.H^2O$, obtained by precipitating a solution of the neutral barium-salt with nitrate of silver, is uncrystallisable (**Svanberg** and **Eckmann**). According to **Cailliot**, it dissolves very slightly in boiling water, and separates therefrom in needles.—The *acid silver-salt*, $C^7H^9AgO^4$, obtained by precipitating the acid ammonium- or barium-salt with nitrate of silver, then evaporating, and leaving the solution to cool slowly, forms beautiful shining prisms.

TEREBIC ETHERS. Terebic acid, as already observed, forms acid ethers, which react like monobasic acids; they are prepared by the direct action of terebic acid on the several alcohols.—*Ethyl-terebic acid*, $C^7H^9(C^2H^5)O^4 = \left.\begin{matrix}C^7H^8O^2\\C^2H^5\\H\end{matrix}\right\}O^2$, is an oil, having a burning but not acid taste, sparingly soluble in water, and not capable of being distilled without decomposition. Its salts have but little stability, and are resolved by the slightest heat into metallic terebate, ethyl-terebic acid, and alcohol, *e.g.*:

$$C^{14}H^{16}Ba''(C^2H^5)^2O^8 + H^2O = C^7H^8Ba''O^4 + C^2H^6O + [C^7H^9(C^2H^5)O^4].$$

The *methylic* and *amylic ethers* resemble the ethylic ether in composition and in properties. (Cailliot, *loc. cit.*)

TEREBILIC ACID. Syn. with TEREBIC ACID.

TERECAMPHENE. An isomer of turpentine-oil (*q.v.*).

TERECHRYSIC or **TERECRYLIC ACID.** $C^6H^8O^5$. An acid said by Cailliot to be contained, together with oxalic, terephthalic, terebenzic, and turpentinic acids, in the watery liquid obtained by oxidising turpentine-oil with nitric acid diluted with an equal bulk of water.

TERENITE. A mineral from Antwerp, in New York, of specific gravity 2·53, regarded by Dana (ii. 203) as an altered form of scapolite.

TEREPHTHALAMIDE. See TEREPHTHALIC AMIDES (p. 726).

TEREPHTHALIC ACID. $C^8H^6O^4 = \left.\begin{matrix}(C^8H^4O^2)''\\H^2\end{matrix}\right\}O^2$. *Insolinic Acid.*—A product of the oxidation of turpentine-oil and other hydrocarbons and of certain aldehydes. It was discovered by Cailliot (Ann. Ch. Phys. [3], xxi. 28), who obtained it by the action of nitric acid on turpentine-oil, and more completely examined by De la Rue and Hugo Müller (Ann. Ch. Pharm. cxxi. 86). Hofmann (*ibid.* xcvii. 197), by oxidising cuminic acid, cuminic aldehyde, and cymene with chromic acid, obtained a dibasic acid, which he called insolinic acid, and represented by the formula $C^9H^8O^4$, but, according to De la Rue and Müller, this acid is identical with terephthalic acid. According to Schwanert (*ibid.* cxxxii. 257), terephthalic acid is produced by the action of nitric acid upon several volatile oils: cymene, turpentine-oil, lemon-oil, thymene, and cajeput-oil, oxidised with nitric acid, yield terephthalic and camphretic acids; cumin-oil yields terephthalic but no camphretic acid; camphor, wormwood-oil, borneol, and peppermint-oil yield camphretic but no terephthalic acid; thymol does not yield either of these acids; thyme-oil or thymene yields, together with terephthalic acid, an oil having the composition of Hofmann's insolinic acid. De la Rue and Müller (*ibid.* cxx. 339; cxxi. 86) have obtained terephthalic acid, together with other acids, by the action of dilute nitric acid on rectified coal-tar oil (a mixture of toluene, xylene, and pseudocumene), and on the liquid hydrocarbons of Burmese naphtha; they find also that it is always produced in the preparation of toluylic acid from cymene, and in the treatment of that hydrocarbon with fuming nitric acid for the production of nitrotoluylic acid, the result being the same whether the cymene has been obtained from Roman cumin-oil or from camphor. According to Beilstein (*ibid.* cxxxiii. 32; cxxxvii. 301), xylene oxidised with dilute nitric acid yields only toluylic acid: $C^8H^{10} + O^3 = C^8H^8O^2 + H^2O$; but when treated with sulphuric acid and potassic dichromate, it yields, by further oxidation, terephthalic acid, which indeed is likewise produced by the direct treatment of toluylic acid with the same oxidising mixture.

Preparation.—1. From *Turpentine-oil.*—The oil is treated, in a retort, with a large excess of nitric acid diluted with an equal bulk of water, as long as red fumes continue to escape. The acid mother-liquor thus obtained is separated from the resin, and the residue is treated with cold water, which again leaves an orange-yellow resin, containing terephthalic and terebenzic acids. The latter may be removed by solution in cold alcohol and boiling water; the terephthalic acid is then dissolved in ammonia; and the resulting ammonium-salt, after being purified by repeated crystallisation, and boiling with animal charcoal, is decomposed by a mineral acid.

2. From *Cuminic Acid, Cuminic Aldehyde, Xylene*, &c.—One part of cuminic acid is cohobated for about twelve hours with 1 pt. of dichromate of potassium, 8 pts. of strong sulphuric acid, and 12 pts. of water. Terephthalic acid is then found floating on the green liquid, after cooling, as a white flour-like powder, and the liquid retains in suspension a greenish half-fused mass, consisting of chromic terephthalate. The liquid is now to be filtered, the insoluble matter washed with water to remove the soluble chromium-salt, and the residue boiled with ammonia, which dissolves terephthalic acid, leaving chromic oxide undissolved. The ammoniacal solution saturated with hydrochloric acid yields a white powder,

which, when repeatedly boiled with water, or heated with boiling alcohol (to remove adhering cuminic acid), constitutes pure terephthalic acid (Hofmann). In a similar manner terephthalic acid may be prepared from Roman cumin-oil, which is a mixture of cuminic aldehyde and cymene. Beilstein prepares it by boiling 100 grms. xylene for several days with 400 grms. potassium-dichromate and 550 grms. oil of vitriol diluted with twice its weight of water,—then filtering, dissolving the residue in carbonate of sodium, diluting with a large quantity of water, and precipitating with hydrochloric acid.

Properties.—Terephthalic acid is a white, tasteless, crystalline powder, not perceptibly soluble in water, alcohol, ether, chloroform, or acetic acid. When warmed with strong sulphuric acid, it dissolves in considerable quantity, without formation of a sulphoterephthalic acid, and is separated in its original state on addition of water. When heated, it sublimes without previous fusion, forming an indistinctly crystalline sublimate, which has the same composition and properties as the original acid; terephthalic acid is not therefore, like its isomer, phthalic acid, resolved by heat into water and the anhydride. When heated with potash, it is resolved, like phthalic acid, into benzene and carbonic anhydride (De la Rue and Müller). Hofmann's insolinic acid melts at a very high temperature, its melting- and boiling-points nearly coinciding. When distilled, it partly sublimes unaltered, while the rest is decomposed, with formation of benzoic acid and benzene, carbonic anhydride being evolved, and a carbonaceous residue remaining in the retort.*

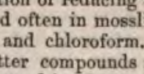
Terephthalates.—Terephthalic acid dissolves in alkalis, neutralising them completely, and is precipitated from its salts by phthalic acid. Although dibasic, it does not form any double salts, and shows but little tendency to form acid salts. Nearly all the terephthalates are soluble and crystallisable, and so inflammable that they may be set on fire by a spark from flint and steel, and burn away slowly like tinder, emitting the characteristic odour of benzene. Terephthalic acid forms acid and neutral ethers (p. 727).

Terephthalate of Ammonium, $C^8H^4(NH^4)^2O^4$, crystallises, by slow evaporation, in small crystals having a strong lustre (Beilstein).—The *barium-salt*, $C^8H^4Ba''O^4.4H^2O$, obtained by mixing the concentrated solution of the ammonium-salt with chloride of barium, crystallises from water in concentrically-grouped tablets, which become anhydrous at 150°, and dissolve in 355 pts. water at 5°.—The *calcium-salt*, $C^8H^4Ca''O^4.3H^2O$, prepared in like manner, dissolves in 1213 pts. water at 6° (Beilstein).—The *silver-salt*, $C^8H^4Ag^2O^4$, separates as a curdy precipitate on mixing the solution of the ammonium-salt with nitrate of silver. (De la Rue and Müller.)

Nitroterephthalic Acid, $C^8H^5(NO^2)O^4$, is formed by the action of a mixture of fuming sulphuric and nitric acids on terephthalic acid, and separates from water in cauliflower-like aggregates. It dissolves easily in hot alcohol, forms well-crystallised metallic salts, and crystallisable ethers, which dissolve easily in alcohol and melt at low temperatures. By reducing agents it is converted into oxyterephthalamic or amidoterephthalic acid (*infra*). (De la Rue and Müller.)

OXYTEREPHTHALIC ACID, $C^8H^6O^5$, is produced by the action of nitrous acid on oxyterephthalamic acid. It forms well-crystallised salts, less soluble than the corresponding terephthalates. (De la Rue and Müller.)

TEREPHTHALIC AMIDES. 1. *Terephthalamide*, $C^8H^8N^2O^2 = N^2.H^4.(C^8H^4O^2)''$, produced by the action of ammonia on terephthalic chloride, is a white amorphous body, not dissolved by any solution.—2. *Nitroterephthalamide*, $C^8H^7(NO^2)N^2O^2$, formed by the action of fuming nitric acid on terephthalamide, crystallises in fine prisms.—3. *Terephthalyl-nitrile*, $C^8H^4N^2$, is obtained by treating terephthalamide with phosphoric anhydride, distilling over as a liquid, which solidifies in the neck of the retort. It forms fine prismatic crystals, colourless and scentless, insoluble in water and in benzene, easily soluble in cold alcohol. When boiled with caustic alkalis, it is gradually converted into ammonia and terephthalic acid.



4. *Oxyterephthalamic Acid*, $C^8H^7NO^4 = \left.\begin{matrix}H^3\\(C^8H^3O^2)'''\\H\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$, or *Amidoterephthalic Acid*, $C^8H^5(NH^2)O^4$, is produced by the action of reducing agents on nitroterephthalic acid. It crystallises in thin prisms, and often in mosslike groups of crystals, sparingly soluble in cold water, ether, alcohol, and chloroform. It unites both with acids and with bases; the solutions of the latter compounds are highly fluorescent.

The ethers of oxyterephthalamic acid are formed by the action of reducing agents on those of nitroterephthalic acid.—The *ethylic ether* forms large crystals resembling uranic nitrate; its solutions are strongly fluorescent. Oxyterephthalamic acid is converted by nitrous acid into oxyterephthalic acid.

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* The physical characters of insolinic acid are the same as those of terephthalic acid; but the analyses of the acid and of its salts agree very nearly with the numbers required by Hofmann's formula $C^9H^8O^4$, and differ considerably from those required by the formula of terephthalic acid.

TEREPHTHALIC CHLORIDE, $C^8H^4O^2Cl^2$, is produced, together with phosphoric oxychloride, by the action of phosphoric pentachloride on terephthalic acid at 40°. It forms beautiful crystals, inodorous at ordinary temperatures, but smelling when heated like benzoic chloride, which it resembles in its reactions. (De la Rue and Müller.)

TEREPHTHALIC ETHERS. Terephthalic acid forms both neutral and acid ethers. The neutral ethers are formed by the action of terephthalic chloride upon alcohols, or by that of alcoholic iodides on the silver- or potassium-salt of terephthalic acid.—The acid ethers are usually formed in small quantity, together with the neutral ethers, by the action of alcoholic iodides on terephthalate of silver. They are well-marked monobasic acids, and form salts insoluble in alcohol.

Neutral Amylic Terephthalate, $C^8H^4(C^5H^{11})^2O^4$, forms pearly scales, which melt at the heat of the hand.—The *neutral ethylic ether*, $C^8H^4(C^2H^5)^2O^4$, forms long prismatic crystals resembling urea, and easily soluble in alcohol (De la Rue and Müller). It melts at 44°, solidifies at 29°, is insoluble in water, but dissolves easily in alcohol and ether (Beilstein).—The *neutral methylic ether*, $C^8H^4(CH^3)^2O^4$, forms beautiful flat prismatic crystals, several inches long, which melt at a temperature above 100°, and sublime without decomposition. It dissolves easily in warm, less easily in cold alcohol (De la Rue and Müller). According to Beilstein, it melts at 140°, and solidifies again at 130°.—The *neutral phenylic ether*, $C^8H^4(C^6H^5)^2O^4$, is white, crystalline, and melts at a temperature above 100°. (De la Rue and Müller.)

TEREPHTHALYL-NITRILE. See Terephthalic Amides (p. 726).

TEROPIAMMONE. Syn. with Triopianylamide. (See Opianic Acid, Amides of, iv. 206.)

TERPILENE. See Turpentine-oil, Hydrates of.

TERPIN. }
TERPINOL. } Hydrates of turpentine-oil (*q. v.*).

TERRA CATECHU. Syn. with Catechu (i. 816).

TERRA DI SIENA. A ferruginous clay, occurring near Siena, in Italy, in thick brownish-yellow masses, often light-yellow in the middle, and yielding a greenish-yellow powder. It has a specific gravity of 3·46, a conchoïdal fracture, and adheres strongly to the tongue. According to Rowney, it contains 75·3 per cent. ferric oxide, 9·5 alumina, 11·1 silica, and 13·0 water, besides small quantities of lime and magnesia. When burnt, it becomes brown-red, and yields a dark-red powder. It is used as a pigment, both in its natural state, as *raw siena*, and, after ignition, as *burnt siena*.

TERRA FOLIATA TARTARI. A name of potassium-acetate. Sodium-acetate is sometimes called *Terra fol. tart. crystallisabilis.*

TERRA JAPONICA. Syn. with Catechu.

TERRA LEMNIA. Lemnian earth (iii. 570).

TERRA MIRACULOSA. Obsolete name of bole.

TERRA MURIATICA. Obsolete name of magnesia.

TERRA NOBILIS. A name applied by Bergemann to the diamond, at a time when its real nature was not known.

TERRA PONDEROSA. An old name of baryta. *Terra ponderosa salita*, old name of barium-chloride.

TERRA UMBRA. See Umber.

TERRA VITRESCIBILIS. One of the three elementary earths assumed by Becher, and supposed to be especially abundant in siliceous minerals.

TESSELITE. Syn. with Apophyllite (i. 351).

TESSERAL PYRITES. A name applied to the native arsenides of cobalt, smaltine and skutterudite, both of which crystallise in the monometric or tesseral system (i. 1041).

TETARTINE. Syn. with Albite. (See Felspar, ii. 621.)

TETARTOHEDRY. See Crystallography (ii. 121, 144).

TETRA. A prefix applied to compounds containing 4 at. of a chlorous element to 1 at. of a basylous element: *e.g.*, tetrachloride of tin, $SnCl^4$; also to substitution-compounds, in which 4 at. hydrogen are replaced by a radicle, simple or compound: *e.g.*, tetrachloroquinone, tetramethylammonium, &c.

TETRACLASITE. Syn. with SCAPOLITE (p. 203).

TETRADECYL, or **TETRADECATYL.** $C^{14}H^{29}$; also called *Myristyl.*—The fourteenth term of the series of alcohol-radicles, $C^{n}H^{2n+1}$.—*Tetradecylic hydride,* $C^{14}H^{30}$, is one of the constituents of American petroleum: it boils between 236° and 240°, and is converted by chlorine into the corresponding chloride, $C^{14}H^{29}Cl$.—*Tetradecylic* or *Myristic Alcohol*, or *Methal*, $C^{14}H^{30}O$, is one of the constituents of spermaceti (iii. 1072).

TETRADYMITE. Native telluride of bismuth (p. 707).

TETRAHEDRITE. *Fahl-ore, Grey Copper, Fahlerz, Kupferfahlerz, Panabase.* —Varieties: *Polytelite, Weissgiltigerz* or *Silberfahlerz*; *Schwarzgiltigerz* and *Graugiltigerz*; *Spaniolite* or *Quecksilberfahlerz.*

The name tetrahedrite, or fahl-ore, is applied to a group of isomorphous minerals, crystallising in hemihedral forms of the monometric or regular system, and consisting of mixtures of sulphur-salts (sulphantimonites and sulpharsenites), in which the sulphur of the base is to that of the acid, for the most part, as 4 : 3. The general formula of the group is, therefore, $\left.\begin{matrix} 4(M^2\,;\,N'')S \\ (Sb^2\,;\,As^2)S^3 \end{matrix}\right\}$ or $\left.\begin{matrix} (M^2\,;\,N'')^4 \\ Sb^2\,;\,As^2 \end{matrix}\right\}S^7$, the symbol M denoting Cu (*cuprosum*) and Ag, and N″ denoting Fe, Sn, and Hg (= 200).

The forms of most frequent occurrence are the regular tetrahedron, $\frac{O}{2}$ (*fig.* 190, ii. 230), the triakis-tetrahedron $\frac{2O2}{2}$ (*fig.* 796), and the combinations $+\frac{O}{2} \cdot \infty O\infty$ (*fig.* 197, ii. 231), $+\frac{O}{2} \cdot \infty O$ (*fig.* 203, ii. 232), $+\frac{O}{2} \cdot +\frac{2O2}{2}$ (*fig.* 797), $+\frac{O}{2} \cdot +\frac{2O2}{2} \cdot \infty O$ (*fig.* 798), $+\frac{2O2}{2} \cdot \infty O \cdot \frac{\frac{3}{2}O}{2}$, and others.

Fig. 796.

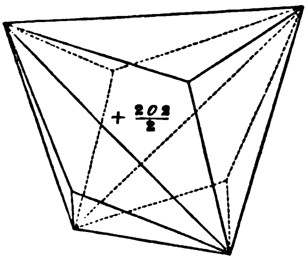
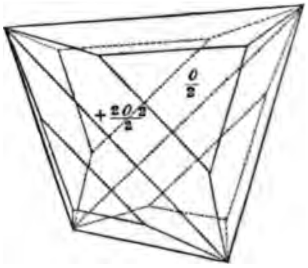
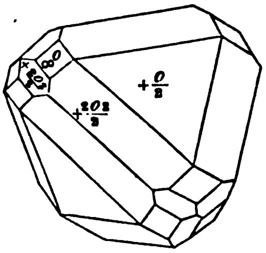


Fig. 797.



Twin-crystals occur, with octahedral composition-face. Cleavage octahedral in traces. The mineral also occurs granular to impalpable, and compact. Hardness = 3 to 4·5. Specific gravity = 4·5 to 5·11. Lustre metallic. Colour between steel-grey and iron-black. Streak generally the same as the colour. Opaque, or subtranslucent in very thin splinters, with cherry-red transmitted colour. Fracture subconchoïdal, uneven. Rather brittle.

Fig. 798.



Before the blowpipe, it gives off fumes of antimony and sometimes of arsenic, then melts, and after roasting leaves a globule of copper. When pulverised, it dissolves with little residue in nitric acid, forming a brownish-green solution.

The best mode of analysing tetrahedrite is that of H. Rose, which consists in heating the mineral in a stream of chlorine; the metals are thereby converted into chlorides, some of which are volatile, while others are fixed, a division which greatly facilitates the further separation (p. 537).

Analyses:—1, 2. H. Rose (Pogg. Ann. xv. 576).—3. Svanberg (Kongl. Vetensk. Acad. Förhl. iv. 85).—4. Rammelsberg (*Mineralchemie*, p. 87).—5, 6, 7. H. Rose, (*loc. cit.*)—8. Genth (Sill. Am. J. xvi. 83).—9. Scheidhauer (Pogg. Ann. lviii. 161).—10. Von Hauer (Jahrb. Geolog. Reichs. 1852, p. 98):—

	S.	Sb.	As.	Cu.	Fe.	Zn.	Ag.	Hg.	
1. Clausthal . . .	24·73	28·24	. .	34·48	2·27	5·55	4·97	. .	= 100·24
2. Freiberg . . .	21·17	24·63	. .	14·81	5·98	0·99	31·29	. .	= 98·87
3. *Aphthonite* Wermland.	30·05	24·77	trace	32·91	1·31	6·40	3·09	. .	Pb 0·04, Co 0·49 gangue 1·29 = 100·37
4. Meiseberg . .	24·80	26·56	. .	30·47	3·52	3·39	10·48	. .	Pb 6·78 = 100·00
5. Kapnik . . .	25·77	23·94	2·88	37·98	0·86	7·29	0·62	. .	= 99·34
6. Gersdorf . . .	26·33	16·52	7·21	38·63	4·89	2·76	2·37	. .	= 98·71
7. Alsace . . .	26·83	12·46	10·19	40·60	4·66	3·69	0·60	. .	quartz 0·41 = 99·44
8. Cabarras, N. Carolina	25·48	17·76	11·55	30·73	1·42	2·53	10·53	. .	= 100
9. *Spaniolite*, Iglo, Hungary	23·34	18·48	3·98	35·90	4·90	1·01	trace	7·52	quartz 2·73 = 97·86
10. „ Poratsch, Hungary.	24·37	25·48	trace	30·58	1·46	. .	0·09	16·69	= 98·58

Most of these analyses agree nearly with the general formula above given.

When the mineral contains much silver, it is called *Polytelite*, *Silberfahl-ore*, or *Weissgiltigerz*. A variety of this mineral, which occurs massive and fine-granular, of specific gravity 5·438 and 5·465, at the "Hoffnung Gottes" mine, near Freiberg, contains 36 to 38 per cent. lead, together with 22·53 S, 22·39 Sb, 5·92—5·73 Ag, 3·72—3·83 Fe, 3·15—6·7 Zn, 0·19—0·32 Cu = 100. In this mineral the sulphur-ratio for the bases and acids is 3 : 2; but it may be regarded as tetrahedrite, if some of the bases are reckoned as impurities.

An ore from mine Altar, near Coquimbo, was found by Field (Chem. Soc. Qu. J. iv. 332) to contain 30·35 per cent. S, 3·91 As, 20·28 Sb, 36·72 Cu, 7·26 Zn, 1·23 Fe, 0·075 Ag, and 0·008 Au. It is soft, of greasy appearance, greenish-grey, slightly reddish, and yields a bright-red powder. Domeyko considers it impure, containing blende, pyrites, and galena. Ettling observes that it is analogous in constitution rather to enargite than to tetrahedrite, corresponding to the formula $4M^2S.(Sb^2; As^2)S^3$.

Aphthonite, or *Aftonite*, from Wermland, Sweden, has a steel-grey colour, and black streak; hardness = 3; specific gravity = 4·87. It gives the formula $7M^2S.(Sb^2; As^2)S^3$.

Annivite is a massive ore from the Anniviersthal in the Valais, containing (after deduction of 9·4 per cent. of quartz) 26·22 per cent. S, 12·10 As, 9·71 Sb, 5·45 Bi, 39·26 Cu, 4·15 Fe, 2·22 Zn = 99·21, which agrees nearly with the formula $3M^2S.(Sb^2; As^2; Bi^2)S^3$; but the mineral does not appear to have been completely examined. Kenngott (*Uebersicht*, 1855, p. 120) regards it as an impure tetrahedrite.

Tennantite, which is a sulpharsenite of copper and iron, isomorphous with tetrahedrite, is by some mineralogists regarded as a variety of the latter; but its composition does not agree with the formula $4M^2S.As^2S^3$, but rather with $7M^2S.2As^2S^3$. (See TENNANTITE, p. 720.)

For a full discussion of the formula of tetrahedrite, see *Rammelsberg's Mineralchemie* (pp. 90—99).

Large tetrahedral crystals of tetrahedrite, having mostly a rough dull surface, are found in the Cornish mines near St. Austel. More brilliant and highly modified crystals occur at Andreasberg in the Harz, Kremnitz in Hungary, Freiberg in Saxony, Kapnik in Transylvania, and Dillenberg in Nassau. (Dana, ii. 82.)

TETRAMERCURAMMONIUM. See MERCURY-BASES, AMMONIACAL (iii. 917).

TETRAMETHYLAMMONIUM. $N(CH^3)^4$.—Most of the compounds of this base have been already described (iii. 999). Stahlschmidt (Pogg. Ann. cxix. 421; Jahresb. 1863, p. 403), by treating tri-iodide of nitrogen, or tri-iodamide, NI^3,[*] with an excess of methylic iodide, has obtained penta-iodide of tetramethylammonium, together with iodoform:

$$2NI^3 + 9CH^3I = 2N(CH^3)^4I^5 + CHI^3 + 2HI.$$

The brown liquid resulting from the reaction, is almost wholly soluble in boiling absolute alcohol; the solution, on cooling, deposits green crystals of the pentaiodide; and the mother-liquor, on further evaporation, yields iodoform.—If the liquid contains free ammonia, protoiodide of tetramethylammonium is likewise formed, and unites with the iodoform, producing the crystalline compound, $C^6H^{14}NI^7 = N(CH^3)^4I.2CHI^3$.

The pentaiodide of tetramethylammonium easily gives up 4 at. of its iodine to alkalis and reducing agents. With aqueous potash, it forms a yellow solution, which contains the protoiodide, together with iodide and iodate of potassium, and, when treated with acids, again yields the pentaiodide.

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[*] Stahlschmidt finds that when a solution of iodine in absolute alcohol, saturated at ordinary temperatures, is mixed with 3 or 4 vols. of strong aqueous ammonia, the resulting precipitate, after thorough washing with cold water, has the composition of tri-iodamide, NI^3; but if the iodine-solution be mixed with 2 or 3 vols. of a saturated solution of ammonia in absolute alcohol, the precipitate, after being well washed with absolute alcohol, consists of di-iodamide, NHI^2.

On mixing a warm, saturated, alcoholic solution of the pentaiodide with aqueous ammonia, or heating the pulverised compound with strong aqueous ammonia, or mixing an alcoholic solution of iodine with iodide of tetramethylammonium and ammonia, a brown-black or dark-green explosive compound is formed, consisting of a compound of tri-iodide of tetramethylammonium with di-iodamide: $C^4H^{13}N^2I^5 = N(CH^3)^4I^3.NHI^2$, or less probably of di-iodide of tetramethylammonium and tri-iodamide, $N(CH^3)^4I^2.NI^3$. This compound may be dried without decomposition, if the drying be carefully conducted; but it explodes easily when touched with a feather, or with oil of vitriol, or when heated above 100°. It is insoluble in water and in dilute alcohol; but hot absolute alcohol dissolves it, apparently with decomposition, and formation of tetramethylammonium-pentaiodide.—*Nitrate of silver* removes all the iodine in the form of silver-iodide. The compound is decomposed by boiling *potash-ley*, with formation of a small quantity of iodoform. With *sulphydric acid* it decomposes in the manner shown by the equation:

$$C^4H^{13}N^2I^5 + 3H^2S = N(CH^3)^4I + NH^4I + 3HI + S^3.$$

Hydrochloric acid also decomposes it, with separation of iodine. (Stahlschmidt.)

TETRAMETHYL-ETHYLENE. When 1 vol. ethylenic bromide is heated with 2 vols. methylic sulphide to 100°, the two bodies gradually unite into a crystalline mass, consisting of tetramethyl-ethylene-sulphobromide, $C^6H^{16}Br^2S^2 = \left.\begin{matrix}(CH^3)^4\\(C^2H^4)''\end{matrix}\right\}\begin{matrix}S^2\\Br^2\end{matrix}$, which dissolves easily in water, and separates therefrom, by evaporation in a vacuum, in well-defined crystals. This compound dissolves in all proportions of hot water, less freely in alcohol, not at all in ether, and is precipitated by ether from the alcoholic solution, in white prisms. When treated with a silver-salt, it forms, together with bromide of silver, a crystallisable very deliquescent compound. With recently precipitated silver-oxide, it yields a caustic alkaline solution, containing the oxide $(CH^3)^4(C^2H^4)S^2O$. The deliquescent hydrochlorate forms, with platinic chloride, the double salt $(CH^3)^4(C^2H^4)S^2Cl^2.PtCl^4$. (Cahours, Compt. rend. lx. 620, 1147; Jahresb. 1865, p. 477.)

TETRANITRONAPHTHALENE. $C^{10}H^4(NO^2)^4$.—Trinitronaphthalene (iv. 15), treated with fuming nitric acid in sealed tubes, is converted into tetranitronaphthalene; and both nitro-compounds, when acted upon by iodide of phosphorus, yield iodides of polyatomic bases, analogous to iodide of picrammonium (iv. 640). (Lautemann and D'Ajuiar, Bull. Soc. Chim. 1864, i. 431.)

TETRAPHOSPHAMIC ACIDS. (Gladstone, Proc. Roy. Soc. xv. 515.)—These are amic acids derived from tetraphosphoric acid, $P^4H^6O^{13}$ (the acid of Fleitmann and Henneberg's phosphates, iv. 537), and produced by the action of water on the compounds of phosphoric oxychloride with ammonia.*—*Tetraphosphotetramic acid*, $P^4(NH^2)^4H^2O^9$, or $\left.\begin{matrix}P^4\\H^{10}\end{matrix}\right\}\begin{matrix}N^4\\O^9\end{matrix}$, is a solid stable body, insoluble in alcohol, but soluble in water, and combining readily with bases, the amount of replaceable hydrogen appearing to vary from 1 to 6 atoms.

Triammoniated Tetraphosphodiamic Acid, $P^4(NH^2)^2(NH^4)^3HO^{11} = \left.\begin{matrix}P^4\\H^5\\(NH^4)^3\end{matrix}\right\}\begin{matrix}N^2\\O^{11}\end{matrix}$, is a viscid liquid, insoluble in alcohol, but very soluble in water. It forms a liquid compound with ammonia, but metallic salts appear to break it up into a variety of bodies. By the action of heat, boiling water, strong acids, or alkaline carbonates, it may be converted into tetraphosphotetramic acid. Among the bodies formed from it when heated alone, is a white substance, insoluble or nearly so in cold water, and having the same composition as ammonium-metaphosphate, PNH^4O^3; this substance is at once transformed, by hot water or dilute acids, into pyrophosphodiamic acid.

Tetraphosphopentazotic Acid, $P^4N^5H^9O^7$, is formed when oxychloride of phosphorus is fully saturated with ammonia, and the resulting mass is heated to about 230°, and washed with cold water. It is an insoluble body capable of decomposing metallic salts, and contains 1 at. of hydrogen replaceable by potassium or ammonium. When treated with slightly acidulated nitrate of silver, it yields a tetrazotic salt, $P^4N^4H^4Ag^2O^7$; which, when decomposed by mineral acids, yields tetraphosphotetramic acid and other compounds. [For the discussion of the rational formulæ of all these compounds, see the original paper above cited.]

TETRAPHOSPHATES. This name may be applied to one of the classes of phosphates discovered by Fleitmann and Henneberg, namely $M^6P^4O^{13}$ (iv. 537).

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* Phosphoric oxychloride absorbs either 2 or 4 molecules of ammonia, forming white solids, probably consisting of sal-ammoniac, mixed, in the one case, with $P(NH^2)Cl^2O$, and in the other with $P(NH^2)^2ClO$. (Gladstone.)

TETRASULPHODIPHENYLENIC ACID. $C^{12}H^6.4H^2SO^4$.—An acid formed, together with trisulphodiphenylenic acid, $C^{12}H^6.3H^2SO^4$, by heating sulphate of diazobenzidine (tetrazodiphenyl) with strong sulphuric acid (iv. 413).

TETRATHIONIC ACID. See SULPHUR, OXYGEN-ACIDS OF (p. 641).

TETRAZODIPHENYL. $C^{12}H^6N^4$. Syn. with DIAZOBENZIDINE (iv. 412).

TETRAZODIPHENYL-AMIDOBENZOL. $C^{24}H^{20}N^8$. Syn. with DIAZOBENZIDINE-ANILINE (iv. 413).

TETRAZODIPHENYLIMIDE. $N^2H^2(C^{12}H^6N^4)^{iv}$.—A compound produced by the action of aqueous ammonia on perbromide of diazobenzidine (iv. 412).

TETRAPHYLINE. Syn. with triphyline. (See PHOSPHATES, iv. 572.)

TETRENE. Syn. with TETRYLENE.

TETRETHYLAMMONIUM. $N(C^2H^5)^4$. Most of the compounds of this base have been already described (ii. 561).—A *chloriodide*, $N(C^2H^5)^4Cl^2I$, is produced by adding aqueous protochloride of iodine to a solution of chloride of tetrethylammonium in dilute hydrochloric acid. On gently heating the liquid, and leaving it to stand, the chloriodide is deposited in large fern-leaf crystals, belonging to the regular system. It is more soluble in dilute hydrochloric acid than in water, which latter causes decomposition. The solution reacts like protochloride of iodine. (W. A. Tilden, Chem. Soc. J. xix. 145.)

The following compounds of tetrethylammonium with metallic acids have been examined by Al. Classen (J. pr. Chem. xciii. 446; Jahresb. 1864, p. 420):

Tungstate, $(C^8H^{20}N)^2O.2WO^3$	deliquescent.
Molybdate, $(C^8H^{20}N)^2O.2MoO^3.3H^2O$	deliquescent.
Stannates, $\begin{cases}(C^8H^{20}N)^2O.6SnO^2.H^2O\\(C^8H^{20}N)^2O.7SnO^2.H^2O\end{cases}$	insoluble quadratic octahedrons.
Neutral chromate, $(C^8H^{20}N)^2O.CrO^3$	not crystallisable.
Dichromate, $(C^8H^{20}N)^2O.2CrO^3$	prismatic crystals.
Arsenate, $(C^8H^{20}N)^2O.As^2O^5$	crystalline.
Antimonate, $2(C^8H^{20}N)^2O.Sb^2O^5$	deliquescent.

Most of these salts are obtained by treating the metallic acid with a solution of the base; the chromate by decomposing chromate of silver with hydrate of tetrethylammonium. When heated, they yield offensive-smelling products, the dichromate decomposing explosively.

TETRYL, or **BUTYL.** C^4H^9.—The fourth alcohol-radicle of the series C^nH^{2n+1}. In the free state, its molecule contains C^8H^{18}, so that it is isomeric, or perhaps identical (iii. 182), with octylic hydride, $C^8H^{17}.H$. It was first isolated by Kolbe (Chem. Soc. Mem. iii. 278; Chem. Soc. Qu. J. ii. 157), who obtained it by the electrolysis of valerianic acid, and named it *Valyl*; Wurtz (Ann. Ch. Pharm. xciii. 112; xcvi. 364) afterwards obtained it by the decomposition of tetrylic iodide, and examined its properties more fully.

Preparation.—1. *By the action of Potassium or Sodium on Tetrylic Iodide.*—100 pts. of tetrylic iodide and 13 or 14 pts. of sodium, are introduced into a flask, provided with an upright condensing-tube kept cool by ice-water. The action begins at ordinary temperatures, with evolution of heat, the sodium swelling up, and gradually becoming covered with a blue crust. As the action slackens it must be accelerated by external heat, and the liquid kept boiling till the blue colour of the sodium has disappeared, and the flask contains a white mass of sodium-iodide saturated with tetryl. The tetryl is then distilled from the flask, and the distillate rectified over sodium, till the metal completely retains its lustre in the boiling liquid, and is no longer attacked. The portion which, in the last rectification, distils over between 105° and 108° is pure tetryl. When potassium is used, a considerable quantity of the tetryl is resolved into tetrylic hydride and tetrylene: $C^8H^{18} = C^4H^{10} + C^4H^8$. (Wurtz.)

2. *By the Electrolysis of Valerianic Acid:*

$$2C^5H^{10}O^2 = C^8H^{18} + 2CO^2 + H^2.$$

—When an electric current of four Bunsen's cells is passed through a cold saturated solution of potassic valerate,—hydrogen, carbonic anhydride, and tetrylene gases are evolved, and an oily liquid rises to the surface, consisting of tetryl and tetrylic valerate. On boiling this liquid with an alcoholic solution of potash, valerate of potassium gradually separates, while the tetryl remains dissolved in the alcoholic liquid, and may be purified by washing with water, drying over chloride of calcium, and rectification. (Kolbe.)

Properties.—Tetryl is a colourless oily liquid, having a faint but agreeable odour, and a slight taste, with burning aftertaste. Specific gravity = 0·694 at 16°

(Kolbe); 0·7135 at 0° (Kopp); 0·7057 at 0° (Wurtz). Its expansion-coefficient (between 11° and 88°), is, according to Kopp:

$$0{\cdot}0012125t + 0{\cdot}00000027933t^2 + 0{\cdot}000000016297t^3.$$

It boils at 108° (Kolbe); at 108·5° (Wurtz); at 106° under a barometric pressure of 745mm. (Kopp), and distils completely without decomposition. Vapour-density = 4·053 (Kolbe); 4·070 (Wurtz); 4·07 and 3·88 (Gr. Williams); the calculated value (C^8H^{18} = 2 vols.) is 3·95.

Tetryl is insoluble in water, but mixes in all proportions with alcohol and ether. None of the tetryl-compounds can be directly prepared from it.—*Chlorine* and *bromine* act upon it, but form substitution-products.—With *pentachloride of antimony* it yields hydrochloric acid and chlorinated products not yet examined.—*Pentachloride of phosphorus* is decomposed by it only after long boiling, with formation of trichloride of phosphorus, chlorinated tetryl, and hydrochloric acid. When the vapours of iodine and tetryl are passed together over *spongy platinum* heated in a tube to 300°, a large quantity of hydriodic acid is formed, together with a small quantity of an iodised organic substance, probably a substitution-product.—*Hydrochloric acid* has no action upon tetryl, either at ordinary temperatures, or at a temperature near that of boiling oil. (Wurtz.)

Tetryl forms compounds with other alcohol-radicles.

Tetryl-ethyl, $C^6H^{14} = C^4H^9.C^2H^5$, obtained by the action of sodium on a mixture of tetrylic and ethylic iodides, has been already described (ii. 525).

Tetryl-amyl, $C^9H^{20} = C^4H^9.C^5H^{11}$, is prepared by decomposing a mixture of tetrylic and amylic iodides with sodium, in the manner described for the preparation of tetryl. The greater part of the resulting liquid distils over between 130° and 140°, and, by repeated fractional distillation, pure tetryl-amyl is obtained as a colourless liquid, boiling at 132°, having a specific gravity of 0·724 at 0°. Vapour-density = 4·46 (calc. = 4·42). (Wurtz.)

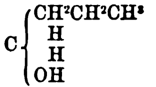
Tetryl-hexyl, $C^{10}H^{22} = C^4H^9.C^6H^{13}$, is obtained by the electrolysis of a mixture of œnanthylate and valerate of potassium. The oily liquid, which collects on the surface of the aqueous solution, is a mixture of several hydrocarbons; and when subjected to fractional distillation, yields, between 100° and 140°, a liquid containing tetryl-hexyl, which, when further rectified, boils between 155° and 160°, and exhibits a vapour-density of 4·917 (calc. = 4·907); but it has not been obtained pure.

TETRYL, ACETATES OF. $C^6H^{12}O^2$.—There are two ethers having this composition, the one corresponding with normal tetrylic alcohol, the other with isotetrylic alcohol (*infra*).

Normal Tetrylic Acetate, $C^4H^9.C^2H^3O^2 = \left.\begin{matrix}C^2H^3O\\C^4H^9\end{matrix}\right\}O$, is produced by distilling equivalent quantities of dry acetate and tetrylsulphate of potassium, or by heating normal tetrylic iodide with a slight excess of silver-acetate in a glass tube, and distilling off the resulting liquid. The distillate is purified by washing with a dilute solution of sodic carbonate, then dried over chloride of calcium, and rectified. It is a colourless liquid, of agreeable odour, specific gravity = 0·844 at 16°, and boiling at 114°. Vapour-density = 4·073; calc. = 4·017. By prolonged boiling with potash, it is resolved into acetic acid and normal tetrylic alcohol. (Wurtz, Ann. Ch. Pharm. xciii. 121.)

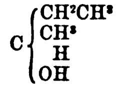
Isotetrylic Acetate, perhaps $C^4H^8\left\{\begin{matrix}H\\C^2H^3O^2\end{matrix}\right.$, is produced, together with tetrylene, by heating isotetrylic iodide (obtained from erythromannite, p. 736), with acetate of silver in sealed tubes. On distilling off the tetrylene, the isotetrylic iodide remains, and may be purified like the normal ether. It is a colourless liquid, boiling at 111° to 113°, and having a strong, agreeable, aromatic odour, but not fruity, like the normal acetate. (De Luynes, Jahresb. 1864, p. 501.)

TETRYL ALCOHOLS. $C^4H^{10}O$.—In the article "SECONDARY AND TERTIARY ALCOHOLS" (p. 216), it is observed that there are three possible tetryl or butyl alcohols, represented by the following formulæ:—



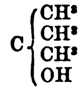
$$C\left\{\begin{matrix}CH^2CH^2CH^3\\H\\H\\OH\end{matrix}\right.$$

Primary.



$$C\left\{\begin{matrix}CH^2CH^3\\CH^3\\H\\OH\end{matrix}\right.$$

Secondary.



$$C\left\{\begin{matrix}CH^3\\CH^3\\CH^3\\OH\end{matrix}\right.$$

Tertiary.

An alcohol having the composition $C^4H^{10}O$, is produced, together with ethylic and amylic alcohols, in the fermentation of sugar, and is found in the fusel-oil obtained from mangold-wurzel, and sometimes in that obtained from potatoes. This, which was discovered by Wurtz in 1852 (Compt. rend. xxxv. 210; Ann. Ch. Pharm. xciii. 107), and is distinguished as normal tetrylic or butylic alcohol, is supposed to be the primary alcohol. An alcohol, most probably identical with it, has been obtained by Schöyen (Ann. Ch. Pharm. cxxx. 233), by heating chloride of tetryl prepared from ethyl (p. 734) with acetate of potassium and glacial acetic acid, whereby it is converted into tetrylic acetate, and distilling this compound ether with baryta-water.

An abnormal tetrylic alcohol (whether secondary or tertiary has not yet been ascertained) is produced by distilling the iodide or the acetate of tetryl, obtained from erythromannite, with potash.

a. *Normal Tetrylic Alcohol*, $C^4H^{10}O = \left.\begin{matrix}C^4H^9\\H\end{matrix}\right\}O$. *Hydrate of Tetryl. Tetrylic Hydrate.* (Wurtz, *loc. cit.*)—This alcohol was first obtained from potato-fusel-oil, in which, however, it is not always present. It is best prepared by subjecting the fusel-oil obtained in the rectification of mangold-wurzel molasses to fractional distillation, the portions which distil over between 80° and 105°, 105° and 115°, 115° and 125°, being collected apart. The first portion is washed with water, and the separated oily layer repeatedly rectified, the portion which passes over at 104° being each time collected apart. The latter is mixed with the portion which distilled over between 105° and 115°, and with that part of the last fraction (between 115° and 125°) which, when the latter was repeatedly rectified, passed over below 115°. The whole of the distillates obtained between 105° and 115° are then mixed together, and boiled for forty-eight hours with a concentrated solution of caustic potash, in such a manner that the vapours may be condensed and allowed to run back again. The impure tetrylic alcohol is then distilled over; separated from the water which passed over with it; afterwards mixed with half its weight of quicklime, to dehydrate it more completely, and distilled off after standing for twenty-four hours; this distillate is repeatedly rectified and the portion which passes over between 108° and 110° is collected apart: if the boiling-point remains within these limits during the distillation, the tetrylic alcohol thus obtained is very nearly pure. The process of rectification may be considerably abridged by interposing between the flask and the condensing apparatus an upright tube with two bulbs, and having a thermometer inserted into its upper part; the less volatile portions then condense on the sides of the tube, and run back into the flask, whereby the separation of the more volatile portions is greatly facilitated. (Wurtz.)

For complete purification, the tetrylic alcohol is converted into iodide of tetryl, which boils at 121°, and is easily separated, by fractional distillation, from iodide of ethyl boiling at 74°, and iodide of amyl at 146°; the iodide of tetryl is converted into acetate by treating it with acetate of silver; the acetate of tetryl decomposed by continued boiling with strong solution of potash, the vapours being condensed and made to run back; and the tetrylic alcohol thereby separated, is deecanted and rectified over caustic baryta.

Properties.—Tetrylic alcohol is a transparent colourless liquid, more mobile than amylic alcohol, and having an odour similar to that of the latter, but less pungent and more vinous. It does not turn the plane of polarisation of light. Specific gravity = 0·8032 at 18·5°. Boiling-point = 10°. Vapour-density, obs. = 2·589; calc. = 2·565.

Tetrylic alcohol dissolves in 1½ times its weight of *water* at 18°, and is precipitated therefrom, as an oily layer, on addition of chloride of calcium, chloride of sodium, or any other easily soluble salt. It dissolves *chloride of calcium*, forming a crystallisable compound; also recently fused *chloride of zinc*, forming a syrupy liquid.

Decompositions.—1. Tetrylic alcohol takes fire on the approach of a burning body, and burns with a bright flame.—2. *Potassium* decomposes it, with evolution of hydrogen, forming tetrylate of potassium, C^4H^9KO.—3. *Caustic potash*, in a state of fusion, converts it into butyric acid, with evolution of hydrogen, and formation of a butyrate, When dropt upon *soda-lime* heated to 250°, it is likewise decomposed, with evolution of hydrogen, and formation of a butyrate.—4. *Hydrochloric acid* heated in a sealed tube with tetrylic alcohol, converts it into chloride of tetryl (p. 734).—5. *Pentachloride* and *oxychloride of phosphorus* likewise convert it into chloride of tetryl.—6. *Bromine* and *phosphorus*, added alternately in small portions, convert tetrylic alcohol into bromide of tetryl, with evolution of hydrobromic acid (p. 734).—7. Similarly, *iodine* and *phosphorus* give rise to the formation of iodide of tetryl (p. 735).—8. *Oil of vitriol* acts violently on tetrylic alcohol, the mixture becoming very hot and strongly coloured, while sulphurous acid is evolved, and an oily layer separates out, consisting chiefly of hydrocarbons polymeric with tetrylene. When the alcohol is rapidly mixed with excess of oil of vitriol, great heat is produced, and gas is given off in small quantity, which may, however, be increased by external heating; it consists chiefly of tetrylene, together with sulphurous and carbonic anhydrides. When tetrylic alcohol is gradually mixed with an equal volume of oil of vitriol, and the vessel kept cool, tetryl-sulphuric acid is produced.—9. Tetrylic alcohol heated with excess of *zinc-chloride* is decomposed, with formation of tetrylene, hydride of tetryl, and other less volatile hydrocarbons.—10. With *chloride of cyanogen*, tetrylic alcohol forms chloride of tetryl and tetrylic urethane:

$$2C^4H^{10}O + CNCl = C^4H^9Cl + C^5H^{11}NO^2. .$$

If the tetrylic alcohol, as is generally the case, contains a little water, carbonate of tetryl and sal-ammoniac are formed at the same time:

$$2C^4H^{10}O + CNCl + H^2O = (C^4H^9)^2CO^3 + NH^4Cl$$

(E. Humann, Ann. Ch. Pharm. xcv. 256).—11. Tetrylic alcohol obtained by fermentation yields, by distillation with *sulphuric acid* and *potassic dichromate*, a mixture of butyric and propionic acids with the corresponding aldehydes (Michaelson, Jahresb. 1864, p. 336). The alcohol obtained by Schöyen from tetrylic chloride, as above mentioned, also yields butyric acid when subjected to the same treatment.

Isotetrylic Alcohol. (De Luynes, Ann. Ch. Pharm. cxxviii. 330, cxxxii. 274; Jahresb. 1863, p. 503; 1864, p. 501.)—This alcohol is produced by the action of moist silver-oxide on isotetrylic iodide (obtained by the action of hydriodic acid on erythromannite, ii. 505), or, better, by heating isotetrylic acetate (obtained by decomposing the iodide with acetate of silver) to 100° for thirty hours. The alcohol then separates as an oily layer on the surface of the liquid, and may be purified by drying with carbonate of potassium, and rectification, finally over lumps of sodium. It is a colourless liquid, having a strong odour and burning taste, a specific gravity of 0·85 at 0°, and boiling at 95°—98° (about 10° lower than the normal alcohol). It mixes in all proportions with *alcohol* and *ether*; dissolves also in *water*, and is precipitated from the solution by carbonate of potassium; it dissolves *chloride of calcium*. It absorbs *hydriodic acid*, forming isotetrylic iodide, identical with that produced by the action of hydriodic acid on erythromannite.—With *bromine* it forms a heavy liquid, which strongly attacks the eyes, and varies in boiling-point from 110° to 158°.

Isotetrylic alcohol, when heated for some hours to 250°, is for the most part resolved into water and tetrylene. The corresponding iodide gives off tetrylene when distilled with alcoholic potash. These isotetryl-compounds, therefore, like the β-hexyl-compounds (iii. 152), with which they are homologous, show a great tendency to give up their olefine. In this respect they appear to react more like compounds of tetrylene than of tetryl, and as such they are, in fact, regarded by De Luynes,—the alcohol as $C^4H^8.H^2O$ or $C^4H^8\left\{\begin{matrix}H\\HO\end{matrix}\right.$; the iodide as $C^4H^8.HI$. But the property of readily giving up the olefine does not afford a decisive argument in favour of this view, inasmuch as the same property is possessed, though in a less marked degree, by the normal alcohols $C^nH^{2n+2}O$, all of which, when treated with oil of vitriol or other strong dehydrating agents, are resolved into water and the olefine.

TETRYL, BROMIDE OF. C^4H^9Br. (Wurtz, Ann. Ch. Pharm. xciii. 114.)—This compound is prepared by the action of bromine and phosphorus on tetrylic alcohol. A few drops of bromine are added to tetrylic alcohol; a small piece of phosphorus thrown in, the liquid being kept cool and shaken till the colour of the bromine is destroyed; the addition of bromide and phosphorus then repeated, and so on continually, till vapours of hydrobromic acid are abundantly evolved, and a quantity of bromine has been added at least equal to that of the tetrylic alcohol. The liquid is then distilled at a temperature not exceeding 100°, and the resulting vapours are passed into a flask containing water, which dissolves the hydrobromic acid, while the impure bromide of tetryl collects at the bottom. The latter is washed with water, dried with a little chloride of calcium, and rectified; that which passes over at 89° is pure bromide of tetryl.

It is an oily liquid, having an ethereal odour, and boiling at 89°. Specific gravity = 1·274 at 16°. Vapour-density, obs. = 4·720; calc. = 4·749.

Potassium decomposes bromide of tetryl, slowly at ordinary temperatures, but violently when heated. When the two substances are heated together in a sealed tube, decomposition begins as soon as the potassium melts, a large quantity of gas (probably tetrylene and tetrylic hydride) being evolved, and the tube exploding with violence.—*Ammonia* acts slowly on bromide of tetryl at ordinary temperatures, forming hydrobromate of tetrylamine. (Wurtz.)

TETRYL, CARBONATE OF. See CARBONIC ETHERS (i. 801).

TETRYL, CHLORIDE OF. C^4H^9Cl. (Wurtz, Ann. Ch. Pharm. xciii. 113.)

Prepared: 1. By the action of hydrochloric acid on tetrylic alcohol. When the alcohol is saturated with hydrochloric acid gas, and the liquid sealed up in a glass tube is heated in the water-bath, a large quantity of chloride of tetryl is produced, and may be obtained pure by washing the product with water, distilling, and separating the portion which goes over between 70° and 75°.—2. By the action of pentachloride or oxychloride of phosphorus on tetrylic alcohol. The alcohol is placed in a flask with a long neck, which must be kept very cool, and the chloride of phosphorus added by small portions. Violent action takes place, attended with great evolution of heat, and the pentachloride is converted into oxychloride, which then acts on the last portions of tetrylic alcohol. The oxychloride may also be used from the beginning instead of the pentachloride, in which case the action is less violent. In either case, the contents of the flask must be left to stand for 24 hours, and then distilled, the portion which passes over below 100° being collected apart; this portion is then washed with water, dried over chloride of calcium, and rectified, collecting separately the portion which distils over at 70°.—3. By the action of chlorine on tetrylic hydride. (Pelouze and Cahours.)

4. By distilling amylic alcohol with calcic hypochlorite (120 grms. amylic alcohol with 1,500 grms. bleaching powder, and 2,500 grms. water). The oily distillate yields, after fractionation, about 20 grms. of a liquid boiling between 62° and 64°; and on treating this with oil of vitriol, and afterwards with potash (to remove chloroform), pure tetrylic chloride is obtained. (F. Gerhard, Ann. Ch. Pharm. cxxii. 363; Jahresb. 1862, p. 409.)

Chloride of tetryl is a liquid lighter than water, and having an ethereal odour, recalling also that of chlorine: specific gravity = 0·88 (Gerhard). Boiling-point about 70°. It is rapidly decomposed by potassium, with rise of temperature and evolution of gas (Wurtz). Chlorine converts it into trichloride of carbon. (Gerhard.)

TETRYL, CYANIDE OF. See Cyanides (ii. 272).

TETRYL, FORMATE OF. See Formic Ethers (ii. 695).

TETRYL, HYDRATE OF. Normal tetrylic alcohol, $C^4H^9.H.O$ (p. 732).

TETRYL, HYDRIDE OF. $C^4H^{10} = C^4H^9.H$.—This compound, discovered by Wurtz (Ann. Ch. Pharm. xciii. 112), is produced, together with tetrylene, by heating tetrylic alcohol with excess of zinc-chloride. When the gaseous mixture thus evolved is passed, first through a tube surrounded with ice and inclined upwards, to condense the less volatile hydrocarbons formed at the same time, and allow them to flow back again —then through a tube surrounded with a freezing mixture, a very volatile, mobile, colourless liquid condenses in this tube, and on being removed from the freezing mixture, quickly evaporates, yielding a mixture of about equal volumes of tetrylene and tetrylic hydride. The tetrylene may be absorbed by a coke-ball saturated with sulphuric anhydride, and tetrylic hydride then remains nearly pure.

Tetrylic hydride is one of the constituents of American petroleum, being found, according to Pelouze and Cahours (Ann. Ch. Phys. [4], i. 5), in the most volatile portion of the oil, boiling between 5° and 10°. Ronalds (Chem. Soc. J. xviii. 54), by subjecting the portion which distilled between 0° and 4° (containing tetrylic hydride with smaller quantities of tritylic and ethylic hydrides), to fractional distillation, and collecting the distillate in a well-cooled receiver, obtained the tetrylic hydride in a state of purity. It is a very mobile liquid, having a sweetish odour, a specific gravity of 0·60 at 0°, and vapour-density = 2·11 (calc. = 2·006). It burns with a yellow, faintly luminous flame, is insoluble in water, but dissolves in alcohol and in ether. Alcohol of 98 per cent. absorbs 11 or 12 times its volume of the vapour. When 1 vol. of the vapour is mixed with 2 vols. chlorine-gas, chloride of tetryl condenses, and 2 vols. hydrochloric acid gas are produced.—The portion of American petroleum distilling between 6° and 8° is a mixture of tetrylic and amylic hydrides. (Ronalds.)

TETRYL, IODIDES OF. *a. Normal tetrylic iodide*, C^4H^9I, is produced by the action of phosphorus and iodine on tetrylic alcohol. 1·5 pt. iodine is added to 1 pt. tetrylic alcohol in a vessel surrounded with cold water, and a quantity of phosphorus equal to about $\frac{1}{10}$ of the iodine, added in successive small portions, the mixture being heated towards the end of the process, to render the action complete. The dark colour of the liquid then gradually changes to brownish-yellow, whilst hydriodic acid is abundantly evolved, which, together with a small quantity of tetrylic iodide that passes over with it, is received in a small quantity of cold water. As soon as the colouring produced by the iodine has disappeared, and the liquid is in full ebullition, it is left to cool, and that which remains in the distillation-vessel is washed, first with the aqueous hydriodic acid previously collected—whereby a small quantity of undecomposed tetrylic alcohol is dissolved—and then with pure water; it is then dehydrated with chloride of calcium, and freed from the still remaining portion of tetrylic alcohol, by treating it while warm with pulverised iodide of phosphorus, till the latter crystallises out on cooling. The liquid is then distilled, and the distillate is washed with water, dehydrated over chloride of calcium, and rectified, the portion which passes over between 118° and 122° being collected.

Tetrylic iodide is colourless when recently prepared, but soon turns brown by exposure to light. It refracts light strongly; boils at 121°; but when a mixture of water and iodide of tetryl is distilled, the thermometer, at the beginning of the distillation, when the tetrylic iodide chiefly passes over, indicates only 88° to 89°. Specific gravity = 1·604 at 19°. Vapour-density = 6·217 (calc. = 6·344).

Tetrylic iodide *burns* with difficulty, and only in contact with a burning body; the combustion is attended with evolution of iodine-vapours. It is but slowly attacked by *aqueous potash*, even when boiled therewith for some time; but *alcoholic potash* decomposes it, with formation of tetrylic alcohol and iodide of potassium.—*Potassium* decomposes iodide of tetryl, yielding tetryl and iodide of potassium.—With *tetrylate of potassium*, C^4H^9KO, it forms tetrylic ether and iodide of potassium (p. 736).—With *oxide of silver*, it forms tetrylic ether and iodide of silver.—With *silver-salts* (*e.g.* the carbonate, sulphate, acetate, &c.) it forms iodide of silver and a compound ether (*e.g.* carbonate, sulphate, acetate, &c.) of tetryl. A solution of nitrate of silver is immediately precipitated by iodide of tetryl. (Wurtz.)

β. *Isotetrylic iodide*, perhaps $(C^4H^8)''\left\{\begin{matrix}H\\I\end{matrix}\right.$. (De Luynes, Jahresb. 1862, p. 479; 1863, p. 503; 1864, p. 500).—This compound is produced by the action of hydriodic acid on erythromannite (ii. 505):

$$C^4H^{10}O^4 + 7HI = C^4H^9I + 4H^2O + 3I^2.$$

Thirty grms. of perfectly dry (fused) erythromannite are slowly distilled with 350 to 400 grms. of fuming hydriodic acid, of specific gravity 1·99. As soon as the liquid boils, isotetrylic iodide distils over, together with undecomposed hydriodic acid. It is purified by washing with potash-ley, then with water, dried over chloride of calcium, and rectified. With weaker acid (of specific gravity 1·70, for example), a greenish product is obtained, which decomposes partially during rectification, and is best purified by a second distillation with hydriodic acid.—2. By the action of hydriodic acid gas on isotetrylic alcohol, &c.

Isotetrylic iodide, when recently prepared, is colourless, and has an agreeable ethereal odour. Its specific gravity is 1·632 at 0°, 1·600 at 20°, and 1·584 at 30°. It boils at about 118°. Vapour-density = 6·597 at 20°; = 6·517 at 24°. It is insoluble in water, but soluble in alcohol and ether. When exposed to light at a somewhat high temperature, it becomes coloured.—*Chlorine* decomposes it, separating iodine, and forming an aromatic liquid, which boils at 120° (probably $C^4H^8Cl^2$).—With *bromine* it gives off iodine, and yields bromide of tetrylene, $C^4H^8Br^2$.

TETRYL, NITRATE OF. $C^4H^9NO^3$. (Wurtz, Ann. Ch. Pharm. xciii. 120.)—Prepared by mixing tetrylic iodide with a small quantity of fused urea, and a slight excess of fused silver-nitrate. The reaction takes place immediately, accompanied by so much heat that part of the product distils over; the rest must be afterwards volatilised, by heating the mixture to 140°—150°. The distillate is purified by washing with slightly alkaline water, drying with chloride of calcium, and rectification.

TETRYL, OXIDE OF. $C^8H^{18}O = (C^4H^9)^2O$. (Wurtz, Ann. Ch. Pharm. xciii. 117.)—Produced: 1. By the action of tetrylic iodide on tetrylate of potassium. The product thus obtained is, however, difficult to purify from tetrylic alcohol, as the boiling-points of the two liquids differ but little from each other.—2. A purer product is obtained by the action of tetrylic iodide on oxide of silver.

Ethyl-tetrylic ether, $(C^2H^5)(C^4H^9)O$, is produced by the action of ethylic iodide on tetrylate of potassium. It is a colourless fragrant liquid, having a specific gravity of 0·7507.

TETRYL, SULPHATE OF. See SULPHURIC ETHERS (p. 629).

TETRYL, SULPHYDRATE OF. $C^4H^{10}S = C^4H^9.H.S$. *Tetrylic* or *Butylic Mercaptan*. (E. Hermann, Ann. Ch. Pharm. xcv. 256; Chem. Soc. Qu. J. viii. 274.)—Produced by distilling, at the heat of the water-bath, a mixture of aqueous sulphydrate of potassium and concentrated aqueous tetrylsulphate of potassium, the product being received in a well-cooled flask:

$$C^4H^9KSO^4 + KHS = C^4H^{10}S + K^2SO^4.$$

The oily liquid which condenses is decanted, placed in contact with chloride of calcium, and distilled, the portion which passes over between 85° and 90° being collected apart.

Tetrylic mercaptan is a colourless very mobile liquid, having the peculiar disagreeable odour which characterises the mercaptans. Specific gravity = 0·848 at 11·5°. Vapour-density = 3·10. Boils at 88°. It has no action on vegetable colours, is very sparingly soluble in *water*, but freely in *alcohol* and *ether*; it dissolves *sulphur* and *iodine*. It is very inflammable, and burns with a pale-blue flame.—Dilute *nitric acid* acts very strongly upon it, forming an oily liquid which floats on the surface.

Potassium decomposes tetrylic mercaptan, with evolution of hydrogen, and formation of a white granular tetrylmercaptide of potassium, C^4H^9KS. Tetrylic mercaptan is also decomposed by several metallic oxides, or by the solutions of their salts, forming tetrylmercaptides: *e.g.* with *mercuric oxide*:

$$2C^4H^{10}S + Hg''O = C^8H^{18}Hg''S^2 + H^2O.$$

The mercury-compound thus obtained forms white nacreous scales, which are unctuous to the touch, and very fusible. It is decomposed by sulphydric acid, with formation of mercuric sulphide and tetrylic alcohol.—The *lead-compound*, $C^8H^{18}Pb''S^2$, is a yellow crystalline precipitate, formed on evaporating an alcoholic solution of tetrylic mercaptan into acetate of lead.—The *cupric* and *auric salts* are white precipitates.

TETRYLAMINE. $C^4H^{11}N = N.H^2.C^4H^9$. *Butylamine.* (Wurtz, Ann. Ch. Pharm. xciii. 124.)—This base, produced by the action of potash on cyanate or cyanurate of tetryl, is metameric with diethylamine, $N.H.(C^2H^5)^2$, ethyl-dimethylamine, $N.C^2H^5.(CH^3)^2$, and methyl-tritylamine, $N.H.CH^3.C^3H^7$. Petinine, a volatile base obtained by Anderson from the most volatile portion of bone-oil, is also isomeric, or perhaps identical, with tetrylamine.

To prepare tetrylamine, 2 pts. of potassic tetrylsulphate are distilled with 1 pt. of recently prepared and perfectly dry potassic cyanate; the pasty mixture of tetrylic cyanate and cyanurate, which distils over, is dissolved in alcohol; and the solution is boiled with fragments of caustic potash. Carbonate of potassium is then formed, and tetrylamine distils over, and is condensed in a small quantity of cold water acidulated with hydrochloric acid. The boiling is continued till the residue fuses completely, and no longer gives off alkaline vapours. The resulting solution of hydrochlorate of tetrylamine is evaporated to dryness; and the residual salt, freed by fusion from the water which it retains, is pulverised when cold, and rapidly mixed with an equal weight of quicklime. This mixture is then introduced into a tube of hard glass, which must be filled with it to about four-fifths; the upper part of the tube is filled with fragments of caustic baryta; a gas-delivery tube, bent at right-angles, is adapted to the larger tube, and made to pass into a small flask surrounded with ice; and the tube is carefully heated in a combustion-furnace, from the closed end onwards. The evolved tetrylamine is then completely dehydrated by the caustic baryta, and condenses in a cooled flask.

Tetrylamine is a transparent colourless liquid, having a strongly ammoniacal and somewhat aromatic odour, and producing dense white fumes with hydrochloric acid. It boils at 69°—70° (petinine at about 70·5°). It dissolves in all proportions of water, alcohol, and ether; the aqueous solution smells like the pure base, and is very caustic; when concentrated it is somewhat viscid.

Salts of Tetrylamine.—Most metallic solutions are precipitated by tetrylamine in the same manner as by ammonia.—The *zinc*, *cadmium*, and *copper* precipitates dissolve in excess of the reagent; gelatinous *alumina* likewise dissolves in excess of tetrylamine; the precipitates formed in solutions of *chromium*, *nickel*, and *cobalt*, are insoluble in excess of tetrylamine.—With *nitrate of silver*, tetrylamine forms a tawny yellow precipitate, easily soluble in excess. Gelatinous *silica* dissolves in tetrylamine, and remains in the pulverulent and amorphous state when the solution is evaporated.

Hydrochlorate of Tetrylamine, $C^4H^{11}N.HCl$, crystallises in deliquescent needles, which melt below 100°; when exposed to the air, it gives off thick white fumes, and volatilises without residue.—The *chloroaurate*, $(2C^4H^{11}N.HCl).AuCl^3$, crystallises on evaporation in rectangular plates of a pale-yellow colour, melting and changing to orange-yellow at 100°.—The *chloroplatinate*, $2(C^4H^{11}N.HCl).PtCl^4$, crystallises by evaporation in beautiful orange-yellow laminæ, soluble in water and in alcohol.

TETRYLENE. C^4H^8. *Butylene, Butyrene, Butene, Valylene, Ditetryl*.—This hydrocarbon was discovered, in 1825, by Faraday (Phil. Trans. 1825, p. 440), who obtained it by compressing the illuminating gas produced by the destructive distillation of fixed oils. Some years later, Kolbe (Ann. Ch. Pharm. lxix. 269) obtained it by the electrolysis of valerianic acid; and Wurtz (Ann. Ch. Pharm. xciii. 107) has shown that it is a frequent product of the decomposition of tetryl-compounds, being formed especially in the dehydration of tetrylic alcohol by strong sulphuric acid or chloride of zinc, and as a secondary product of the action of potassium or silver-oxide on tetrylic iodide, part of the tetryl thereby set free being resolved into tetrylene and tetrylic hydride (p. 735); it is formed also, in small quantity, in the decomposition of amylic alcohol at a red heat. Lastly, De Luynes (Compt. rend. lvi. 1175; Ann. Ch. Phys. [4], ii. 355; Jahresb. 1863, p. 504; 1864, p. 500) has shown that it is produced by decomposing isotetrylic iodide (p. 736) with alcoholic potash or acetate of silver, isotetrylic acetate being also produced in the latter case.

Preparation.—1. From *Oil-gas.*—Faraday obtained tetrylene by subjecting the illuminating gas, which was prepared in London some years ago by decomposing fixed oils at a moderate red heat, to a pressure of 30 atmospheres. 1,000 cubic feet of the gas thus treated yielded about 4 litres of so-called empyreumatic oils, consisting chiefly of tetrylene and benzene. As the former of these hydrocarbons boils below 0°, it may be separated, in great part, by gradually warming the mixture to 38° in a suitable distillatory apparatus connected with a receiver cooled to $-18°$; and by subjecting the distillate several times to the same treatment, but each time at a lower temperature, the tetrylene may be obtained nearly pure.

Tetrylene is also formed by subjecting acetate of sodium or oleate of calcium, mixed with soda-lime, or butyrate of barium, or by itself, to destructive distillation; also by heating glucose with soda-lime; in each case, however, the tetrylene is accompanied by a large quantity of tritylene, amylene, and other hydrocarbons. The gases thus evolved are fixed by passing them through bromine, whereby they are all converted into bromides; and from the mixture thus obtained, the bromide of tetrylene may be separated by fractional distillation. (Berthelot, Ann. Ch. Pharm. cviii. 200.)

2. From *Valerianic Acid.*—A concentrated solution of potassic valerate is subjected to the action of an electric current with platinum electrodes. Tetrylene is then evolved at the positive pole, together with tetryl and carbonic anhydride, while the gas evolved at the negative pole consists wholly of hydrogen; and if a porous diaphragm be interposed between the two electrodes, the tetrylene will pass off, mixed only with tetryl and carbonic anhydride. To separate it, the gaseous mixture is passed, first through a tube surrounded with a frigorific mixture, and through alcohol, to condense and absorb the tetryl; then through water, to take up the alcohol; and lastly through strong potash-ley and over solid potash, to absorb the carbonic acid and water. The tetrylene obtained by this process is merely a secondary product, probably formed by oxidation of a portion of the tetryl, which is the immediate product of the electrolytic action (p. 731):

$$\underset{\text{Tetryl.}}{C^8H^{18}} + O = \underset{\text{Tetrylene.}}{2C^4H^8} + H^2O.$$

3. From *Tetrylic Alcohol.*—When this alcohol is quickly mixed with excess of sulphuric acid, the mixture gently heated, and the evolved gas freed from sulphurous and carbonic acids by absorption with potash, tetrylene is obtained nearly pure, being contaminated only with a small quantity of a hydrocarbon of higher atomic weight.—When tetrylic alcohol is heated with excess of zinc-chloride, nearly pure tetrylene is evolved at first, afterwards a mixture of tetrylene and tetrylic hydride.

4. From *Erythromannite.*—This substance is distilled with hydriodic acid, as already described (p. 736), and the resulting isotetrylic iodide (or tetrylenic hydriodate) is treated with alcoholic potash, or, better, with acetate of silver. The isotetrylic iodide is poured upon an equal weight of silver-acetate, contained in strong glass tubes, which can be quickly sealed; and after the violent reaction which immediately takes place is over, the tubes are cooled in a mixture of ice and salt. On opening them, and exposing them to a gentle heat, gradually raised to 40° or 50°, the whole of the tetrylene is given off, and may either be collected as gas, or condensed in a U-tube cooled to a low temperature. Isotetrylic acetate (p. 734) remains behind in the tubes. (De Luynes.)

Properties.—Tetrylene at $-18°$ is a colourless mobile oil, having an ethereal but peculiar and penetrating odour. At the temperature of a mixture of ether and solid carbonic anhydride, it solidifies to a white crystalline mass, which liquefies again as soon as it is taken out of the freezing mixture (De Luynes). The liquid boils below 0° (Faraday); at $+3°$ (De Luynes). The tension of its vapour at $+15°$ is equal to 4 atmospheres (Faraday). Vapour-density = 1·933 (Kolbe); calc. = 1·940. The gas burns with a red, blue-edged, very smoky flame. It is sparingly absorbed by *water*, easily by *alcohol*, and still more by *ether*: the alcoholic solution gives up the gas, with effervescence, on dilution with water; so likewise does the ethereal solution when diluted, first with alcohol, then with water. It dissolves easily in *glacial acetic acid*, and completely in strong *sulphuric acid*, without formation of sulphurous acid, producing a yellow liquid, from which water separates a light fragrant oil (De Luynes); according to Faraday, the product of this reaction is a conjugated acid [? homologous with ethionic or isethionic acid], which forms peculiar salts. The gas is likewise absorbed by *oils*, both fixed and volatile, *olive-oil* taking up about six times its own volume. It unites with *chlorine* (Faraday; Kolbe), and *bromine* (Hofmann), forming oily products.—Aqueous *hydriodic acid*, saturated at 0°, quickly absorbs tetrylene-gas, forming isotetrylic iodide or tetrylenic hydriodate, C^4H^9I, identical with that produced by the action of hydriodic acid on erythromannite. (De Luynes.)

TETRYLENE-DIAMINE. $C^4H^{12}N^2 = N^2\left\{\begin{matrix}(C^4H^8)'' \\ H^4\end{matrix}\right.$.—A base produced by the action of nascent hydrogen (evolved from tin and hydrochloric acid) upon cyanide of ethylene: $C^2H^4C^2N^2 + H^8 = C^4H^{12}N^2$. It boils above 140°, and its chloroplatinate contains 39·45 per cent. platinum, agreeing with the formula $C^4H^{12}N^2.H^2Cl^2.PtCl^4$. (T. Fairley, Chem. Soc. J. xvii. 362.)

TETRYLENIC ACETATE. $C^8H^{14}O^4 = \left.\begin{matrix}(C^4H^8)'' \\ (C^2H^3O)^2\end{matrix}\right\}O^2$.—Prepared by distilling bromide of tetrylene with acetate of silver. The distillate is purified by repeatedly rectifying the portion which distils above 140°, over dry acetate of silver, and finally by itself, the portion which passes over above 190° being collected apart. Acetate of tetrylene is a colourless oily liquid, inodorous in the cold, but smelling slightly of acetic acid when warmed. It boils at about 200°, is insoluble in water, but dissolves readily in alcohol and in ether. It is easily decomposed by alkalis, with separation of tetrylenic alcohol. (Wurtz.)

TETRYLENIC ALCOHOL. $C^4H^{10}O^2 = \left.\begin{matrix}(C^4H^8)'' \\ H^2\end{matrix}\right\}O^2$. *Tetryl-* or *Butyl-glycol.* (Wurtz, Ann. Ch. Phys. [3], lvi. 412.)—A diatomic alcohol, homologous with ordinary glycol, and produced in like manner, by heating tetrylenic acetate with potash. It is a colourless, viscid, inodorous liquid, having a mild aromatic taste. Specific gravity = 1·048 at 0°. Boiling-point = 183°—184°. Vapour density, obs. = 3·19; calc. = 3·12. It dissolves in all proportions of *water*, *alcohol*, and *ether*.

Tetrylenic alcohol is easily oxidised by *nitric acid*; when heated with dilute nitric acid, it yields oxalic acid. When dilute nitric acid is cautiously poured upon the aqueous solution of the alcohol, so that the two liquids may mix and react slowly, butylactic acid, or oxybutyric acid, $C^4H^8O^3$ (i. 688), is formed, together with another acid, whose calcium-salt is insoluble in water (the silver-salt of the latter yielded 9·2 per cent. carbon and 1·1 hydrogen).—Tetrylenic alcohol, heated with *hydrate of potassium* or *sodium*, is decomposed, with evolution of hydrogen, but not so readily as ordinary glycol. Oxalic acid appears to be formed in this reaction. Succinic acid is not found among the products of oxidation, either by nitric acid or by hydrate of potassium.

Tetrylenic alcohol heated with *hydriodic acid*, is converted into tetrylic iodide, the glycol being first reduced to tetrylic alcohol, according to the equation:

$$C^4H^{10}O^2 + 2HI = C^4H^{10}O + H^2O + I^2,$$

and the tetrylic alcohol converted into tetrylic iodide by the further action of the hydriodic acid. (Wurtz, Ann. Ch. Phys. [3], lxiii. 124.)

TETRYLENIC BROMIDE, $C^4H^8Br^2$, is formed on mixing tetrylene-gas with bromine-vapour, also (according to De Luynes) by the action of bromine on isotetrylic iodide, C^4H^9I, the reaction being attended with evolution of iodine and hydrobromic acid. It is an oily liquid, boiling at 158° (Wurtz; De Luynes), and, according to Cahours (Compt. rend. xlvi. 244), is resolved, by heating with alcoholic ammonia, into bromide of ammonium and bromotetrylene, C^4H^7Br.

TETRYLENIC CHLORIDE. $C^4H^8Cl^2$.—Produced by the direct combination of chlorine and tetrylene gases in diffused daylight, the tetrylene being kept in excess.

The oily product, after being freed from hydrochloric acid, by washing it, first with very weak potash, then with pure water, is dried over chloride of calcium, and distilled, the portion which passes over below 130° being collected apart; and this portion is subjected several times to fractional distillation, till an oil is obtained, boiling constantly at 125° (Faraday; Kolbe). The same compound is probably formed by the action of chlorine on isotetrylic iodide (p. 736), the liquid thus obtained boiling at 120°. (De Luynes.)

Chloride of tetrylene is a colourless oil, having an agreeable sweetish odour, like that of Dutch liquid, and a burning taste. Specific gravity = 1·112 at 28°. Boiling-point = 123°. Vapour-density = 4·426 (Kolbe); by calculation, 4·39. It is insoluble in water, but mixes with alcohol and ether. It burns brightly in the flame of a spirit-lamp emitting smoke mixed with vapours of hydrochloric acid. It is decomposed by heating with alcoholic potash, yielding chloride of potassium and a volatile oily liquid, probably consisting of chlorotetrylene, C^4H^7Cl.

The less volatile portions of liquid, boiling above 130°, which remain behind in the rectification of tetrylenic chloride, are probably also substitution-products, formed simultaneously with the tetrylenic chloride. The same bodies are obtained when chloride of tetrylene is exposed to sunshine in contact with excess of chlorine. A viscid mass is then formed, which still contains hydrogenated products, and does not yield any crystals of trichloride of carbon. (Faraday.)

Tetrylene-gas is likewise absorbed in large quantity by pentachloride of antimony; and on distilling the product, a chlorinated oil is obtained, having the composition $C^4H^7Cl^3$, or $C^4H^7Cl.Cl^2$.

TETRYL-GLYCOL. Syn. with Tetrylenic Alcohol.

TETRYLIN-TRIAMINE. $C^4H^{13}N^3 = N^3\left\}\begin{matrix}(C^4H^7)''' \\ H^6\end{matrix}\right.$.—A triatomic base produced by the action of nascent hydrogen (evolved by the action of tin on hydrochloric acid) upon cyanoform:

$$CH.C^3N^3 + H^{12} = C^4H^{13}N^3.$$

It boils at a temperature above 150°, and forms a platinum-salt containing $2(C^4H^{13}N^3.3HCl).3PtCl^4$. (Fairlie, Chem. Soc. J. xvi. 362.)

TETRYL-ŒNANTHYL. $C^4H^9.C^7H^{13}O$. *Tetryl-œnanthol. Butyl-œnanthyl. Butyl-butyrone.* (See Butyrone, i. 698.)

TETRYLSULPHURIC ACID. $C^4H^9.H.SO^4$. See Sulphuric Ethers (p. 629).

TETRYLSULPHYDRIC ACID. $C^4H^9.H.S$. *Tetrylmercaptan* (p. 736).

TEUCRIUM. The herb of several species belonging to this genus, formerly used in medicine, contains a peculiar, resinous, bitter principle. *T. Polium* is said to be used in Greece as a remedy against the bites of serpents. (Landerer, Buchn. Repert. xcii. 246).

TEUTLOSE (from τεῦτλον, beet).—A kind of sugar, resembling glucose, said to exist, under certain circumstances, in the juice of beet. According to Michaelis (J. pr. Chem. lxxiv. 397), the sugar, sometimes optically inactive, sometimes lævorotatory, produced from the cane-sugar of beet, especially when the juice is acid, is different from ordinary inverted sugar (p. 465).

TEXALITE. A name applied by R. Hermann (J. pr. Chem. lxxxii. 368) to native magnesium-hydrate, $Mg''H^2O^2$, occurring at Woods Mine, Texas, Lancaster County, Pennsylvania, in monoclinic forms homœomorphous with epidote, whereas the ordinary form of magnesium-hydrate (brucite), is rhombohedral; but, according to Auerbach's observations of the polarising properties of the so-called texalite crystals, they also belong to the hexagonal system. (Jahresb. 1861, p. 979.)

TEXASITE. $Ni''CO^3.2Ni''H^6O^4$. Syn. with Emerald-nickel. (See Carbonates, i. 789.)

THIACETONE. One of the compounds, or rather mixtures, obtained, according to Zeise, by the action of ammonia and sulphur on acetone (i. 28).

THALITE. A name applied by D. Owen (Sill. Am. J. xiii. 420), to an altered soapstone from the north shore of Lake Superior, which he supposed to contain a peculiar earth, *thalia*; this however, according to Smith (*ibid.* xvi. 95), and Genth (*ibid.* xvii. 130), was merely impure magnesia.

THALLEIOCHIN, or **DALLEIOCHIN.** A product of the action of chlorine-water on sulphate of quinine (p. 18).

THALLITE. Syn. with Epidote.

THALLIUM. *Atomic weight*, 204; *Symbol*, Tl.—An element discovered by Crookes, in 1861, in a seleniferous deposit from the sulphuric acid manufactory in Tilkerode, in the Harz. In the distillation of some impure selenium prepared from this deposit, a considerable residue was left, which was at first supposed to contain tellurium, till spectrum-analysis showed that a new element was present, whose spectrum consisted of a single sharp and brilliant green line (hence the name thallium, from θαλλός, a green bud). This element was at first suspected to be a metalloïd, but further examination proved it to be a true metal. It was first obtained, in a distinct metallic form, by Crookes, towards the end of the year 1861, and soon afterwards by Lamy, whose experiments appear to have been made without previous knowledge of Crookes's results.* It has since been made the subject of numerous researches, and a great number of its compounds have been prepared and carefully examined. A full account of the results obtained down to January 1864, together with a list of memoirs, is given by Crookes, in the *Journal of the Chemical Society*, vol. xvii. p. 112. The most important papers on thallium and its compounds, published since that date, are the following:—

On the Extraction of Thallium.—Schrötter, Wien. Akad. Ber. xlviii. [2], 734.—

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* Respecting the controversy about the priority of the discovery of the metallic nature of thallium, see Jahresb. f. Chem. 1862, p. 177.

G. Werther, J. pr. Chem. xci. 385.—Streng, Zeitschr. f. Chem. 1865, p. 106.—Bunsen, Ann. Ch. Pharm. cxxxiii. 108.—Willm, Ann. Ch. Phys. [4], v. 5.

Crystalline forms of Thallium-salts.—W. H. Miller, Proc. Roy. Soc. xiv. 555.

Solubility of Thallium-salts.—Crookes, Chem. News. x. 27.

Chlorides of Thallium.—Werther, J. pr. Chem. xci. 385.—Nicklès, Compt. rend. lviii. 537.—Hebberling, Ann. Ch. Pharm. cxxxiv. 11.—Willm, *loc. cit.*

Bromides and Iodides of Thallium.—Werther, *loc. cit.*—Willm, *loc. cit.*—*On the Bromides* also, Willm, Bull. Soc. Chim. 1864. ii. 89.—Nicklès, *loc. cit.*

Fluorides of Thallium.—Kuhlmann, Compt. rend. lviii. 1037.—Buchner, J. pr. Chem. xcvi. 404.

Oxides and Oxygen-salts of Thallium.—(Schönbein, J. pr. Chem. xciii. 35.—Werther, *loc. cit.*—Kuhlmann, *loc. cit.*—Strecker, Ann. Ch. Pharm. cxxxv. 207.—Willm, *loc. cit.*: also, Bull. Soc. Chim. 1866, ii. 165.—*On the Phosphates of Thallium*, Lamy, Ann. Ch. Phys. [4], v. 410.

The memoir of Willm, above referred to, contains a summary of the results relating to thallium and its compounds down to 1865. (See also Jahresb. f. Chemie, 1864, pp. 245—257; 1865, pp. 242—255.)

Sources.—As sulphide, thallium is very widely distributed as a constituent of iron- and copper-pyrites. Amongst those ores in which it occurs most abundantly (although in these cases it does not constitute more than from the 100,000th to the 4,000th bulk of the ore), may be mentioned iron-pyrites from Theux near Spa in Belgium, from Namur, Philipville, Alais, the South of Spain, France, Ireland, Cornwall, Cumberland, and different parts of North and South America; in copper-pyrites from Spain, as well as in crude sulphur prepared from this ore; in blende and calamine from Theux; in blende, calamine, metallic zinc, sulphide of cadmium, metallic cadmium, and cake-sulphur from Nouvelle-Montagne; in native sulphur from Lipari and Spain; in bismuth, mercury, and antimony ores, as well as in the manufactured products from these minerals (frequently in so-called pure medicinal preparations of these metals); in commercial selenium and tellurium (probably as selenide and telluride).

Thallium is likewise frequently present in copper and in commercial salts of that metal. In Spain a very impure copper is prepared by allowing copper-pyrites to oxidise in the air, washing out the resulting sulphate of copper, and placing scrap-iron in the liquid, which causes the copper to precipitate in the powdery state. The metal is then collected together, dried, strongly compressed, and heated to the melting-point. It is brought over to this country in the form of rectangular cakes, weighing about 20 lbs. each. The sulphide of thallium, oxidising to sulphate along with the sulphide of copper, is washed out by the water, and precipitated with the copper by the iron. The two metals readily alloy together.

Thallium is also present in tolerable quantity in lepidolite from Moravia, and in mica from Zinnwald (Schrötter). It has likewise been found in the deliquescent "Sel-a-Glace" from the mother-liquors of the saltworks at Nauheim. This consists of a mixture of the chlorides of magnesium, potassium, and sodium, with relatively considerable quantities of rubidium- and cæsium-chlorides, and sensible traces of thallium-chloride. (Böttger.)

Many samples of commercial sulphuric acid and yellow hydrochloric acid contain thallium. The source in these cases is evidently the pyrites used in the sulphuric acid works.

Preparation.—*a. From Iron Pyrites.*—The pyrites from the Société Anonyme de Rocheux et d'Oneux, Theux, contains about 1 pt. of thallium in 4,000. Two tons of this ore were worked in the following manner:—

The pyrites, broken up into pieces of the size of a walnut, is distilled in hexagonal cast-iron pipes, closed at one end, and arranged in a reverberatory furnace. Conical sheet-iron tubes are luted on to the open ends, and the retorts are kept at a bright-red heat for about four hours. At the end of the operation, the receivers are found to contain from 14 lbs. to 17 lbs. of dark-green or grey-coloured sulphur for every 100 lbs. of ore used. The whole of the thallium originally in the pyrites is found in this sulphur. The sulphur may be dissolved out by means of carbonic disulphide, which leaves the sulphide of thallium behind; or it may be extracted by boiling with caustic soda. The former plan occasions less loss of thallium, but, owing to the inconvenience of working with large bulks of of carbonic disulphide the soda process is preferable. 12 lbs. of caustic soda, 18 lbs. of the thalliferous sulphur, and 1½ gallon of water, are boiled together till the sulphur has disappeared; 6 gallons of water are added; and the clear liquid, when cool, is decanted from a voluminous black precipitate, which has been separated from the sulphur. The precipitate is then collected on a calico filter and washed. It contains the greater portion of the thallium in the form of sulphide, together with iron, copper, mercury, zinc, &c. Some thallium, however, is dissolved in the alkaline liquid and lost. The black precipitate is then dissolved in hot dilute sulphuric acid, to which a little nitric acid is added, and the liquid is diluted with water and filtered. Hydrochloric acid and sulphite of sodium will now throw down the nearly insoluble white protochloride of thallium, which is to be filtered off and washed. (Crookes.)

β. *From Sulphur or Pyrites in the Wet Way.*—The material is dissolved in nitromuriatic acid, until nothing but bright-yellow sulphur is left; water is then added, and the filtrate is evaporated with sulphuric acid, until it is nearly dry, and sulphuric vapours are copiously evolved. The residue is dissolved in a large excess of hot water, and carbonate of sodium is added to alkaline reaction, and then cyanide of potassium (free from sulphide of potassium). The liquid is then heated gently for some time, and filtered. The precipitate contains the whole of the lead (and bismuth) which may be present, as carbonates, whilst the thallium remains in solution. A current of sulphuretted hydrogen being now passed through the liquid, precipitates all the thallium, whilst the copper, antimony, tin, and arsenic remain dissolved. The precipitated sulphide is filtered off, washed, and dissolved in dilute sulphuric acid, and the thallium is precipitated as chloride, by means of hydrochloric acid. (Crookes.)

γ. *From the Flue-dust of Pyrites-burners.*—This is by far the most economical source of thallium at present known. In burning thalliferous pyrites for the purpose of manufacturing sulphuric acid, the thallium oxidises together with the sulphur, and is driven off by the heat. If the passage leading from the burners to the leaden chambers is only a few feet long, the greater portion of the thallium escapes condensation, and volatilises into the leaden chambers; it there meets with aqueous vapour, sulphurous and sulphuric acids, and becomes converted into thallious sulphate. This being readily soluble, both in water and dilute sulphuric acid, and not being reduced by contact with the leaden sides, remains in solution, and accompanies the sulphuric acid in its subsequent stages of concentration, &c. If, on the other hand, the passage connecting the burners and chambers is 10 or 15 (or more) feet in length, nearly the whole of the thallium is condensed, together with a considerable number of other bodies which constitute "flue-dust,"—namely mercury, copper, arsenic, antimony, iron, zinc, cadmium, bismuth, lime, and selenium, together with ammonia, sulphuric, nitric, and hydrochloric acids. The amount of thallium in these flue-deposits is very various, seldom amounting to as much as ¼ per cent., although in some as much as 8 per cent. has been found.

The following is the plan adopted by Crookes for extracting the metal from this dust on the large scale:—The dust is first mixed in wooden tubs with an equal weight of boiling water, and is well stirred; during this operation a considerable quantity of nitrous acid is evolved; after which the mixture is allowed to rest for 24 hours for the undissolved residue to deposit. The liquid is then syphoned off, and the residue is washed, and afterwards treated with a fresh quantity of boiling water. The collected liquors, which have been syphoned off from the deposit, are allowed to cool, precipitated by the addition of a considerable excess of strong hydrochloric acid, and the precipitate, consisting of very impure chloride of thallium, is allowed to subside. The chloride obtained in this way is then well washed on a calico filter, and afterwards squeezed dry. Three tons of the dust yielded 68 pounds of this rough chloride (Crookes). For the further treatment see below.

Werther boils the flue-dust repeatedly with carbonate of sodium; precipitates the filtrate with excess of ammonium-sulphide; converts the precipitate into sulphate by boiling it with sulphuric acid, with addition of a little nitric acid; precipitates the ammoniacal solution of the latter with iodide of potassium; and reduces the iodide of thallium by fusion with cyanide of potassium.

δ. *From Commercial Hydrochloric Acid.*—Many samples of yellow hydrochloric acid contain thallium. It may be separated by neutralising with ammonia, and adding sulphide of ammonium. The black precipitate contains the thallium, together with iron and some other metallic impurities of the acid. It is to be dissolved in sulphuric acid, and the thallium precipitated by hydrochloric acid as protochloride.

The crude protochloride of thallium obtained by either of the above methods is added, by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred, and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused acid sulphate is now to be dissolved in an excess of water, and an abundant stream of sulphuretted hydrogen passed through the solution. The precipitate, which may contain arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free sulphydric acid is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron and alumina, which generally appears in this place, is filtered off;

and the clear solution evaporated to a small bulk. Sulphate of thallium then separates out on cooling, in long, clear, prismatic crystals. As sulphate of ammonium is much more soluble than sulphate of thallium, the latter can readily be separated from the small quantity of the former salt present. The two salts do not crystallise together.

In order to avoid the inconvenience of driving off the excess of oil of vitriol in the decomposition of chloride of thallium, it may in some cases be preferable to proceed as follows:—Boil the chloride of thallium in solution of sulphide of ammonium for five minutes: decomposition takes place readily. Filter, and wash with hot sulphuretted water till no more chlorine can be detected in the filtrate; then dissolve the sulphide on the filter in dilute sulphuric acid, and treat the solution with ammonia, &c., as above directed. (Crookes.)

ε. *From the Saline Residues of the Saltworks at Nauheim.*—The strong solution is mixed with a quantity of platinic chloride not sufficient for complete precipitation, and the precipitate is boiled five or six times with three times its weight of water; the insoluble residue, consisting of the platinum-salts of cæsium, rubidium, and thallium, is boiled with a weak solution of potash and a little hyposulphite of sodium, till a clear solution is obtained; and this solution is treated with cyanide of potassium and sulphydric acid, whereby the thallium is precipitated as sulphide. The liquid is then to be filtered, and the residue washed and dissolved in sulphuric acid. (Böttger.)

ζ. *From Lepidolite and Mica.*—The residue obtained by reduction of the platinum-salts of rubidium, cæsium, and thallium, as described under RUBIDIUM (p. 128), is carefully washed with water, to dissolve the chlorides of cæsium and rubidium; the washed platinum-black is dissolved in nitromuriatic acid, and evaporated to drive off the excess of acid; and the dry mass is digested with water, which leaves the whole of the thallium-chloroplatinate (still containing a little rubidium) undissolved. This residue, after addition of a few drops of hydrochloric acid, is boiled with finely granulated zinc; the excess of zinc is dissolved out of the precipitated metals by hydrochloric acid (which does not take up any thallium); and the washed residue is heated with nitric acid, which dissolves the thallium, and leaves the platinum. (Schrötter.)

η. *From the Mother-liquors of Zinc-sulphate.*—The mother-liquor of zinc-vitriol, obtained at Goslar, in the Harz, by working pyrites from the Rammelsberg, is (according to Bunsen) a very convenient source of thallium. When boiled down to a specific gravity of 1·441 at 24°, it contains (according to an analysis by Neuhoff) 0·05 per cent. chloride of thallium, together with the sulphates of zinc, cadmium, manganese, copper, and many other salts. When mixed with an equal volume of hydrochloric acid, it yields a precipitate of thallium-chloride; and with iodide of potassium, in presence of a sufficient quantity of sodic hyposulphite, a precipitate of thallium-iodide free from copper. The simplest method of obtaining the thallium is to precipitate it, together with copper and cadmium, by immersing plates of zinc in the *cold* liquor. The metallic powder thereby precipitated, after being quickly rinsed, is digested with water containing sulphuric acid; and the resulting solution, containing thallium (together with cadmium), is precipitated with iodide of potassium. A cubic metre of the liquor thus treated yielded 0·6 kilogrm. thallium. (Bunsen.)

θ. To recover the thallium remaining in the mother-liquor of any of the preparations above described, Willm precipitates the solution (reduced, if necessary, by sulphurous acid) with iodide of potassium, decomposes the precipitated iodide of thallium with nitric acid (in a distillatory apparatus, arranged so as to condense the volatilised iodine), and evaporates the resulting solution of thallium-nitrate to the crystallising point. Insoluble residues are treated with nitromuriatic acid, the neutralised solution is precipitated with sulphide of ammonium; and the precipitated sulphide of thallium is converted into sulphate by treatment with sulphuric acid.

Preparation of Metallic Thallium.—The metal is reduced from its solution, generally from the sulphate, either by electrolysis, or by the action of zinc.—1. When an electric current from two or three Grove's cells, with platinum terminals, is passed through an acidulated solution of thallium-sulphate in its own weight of water, the metal is deposited on the negative pole, in brilliant plates and long needle-shaped crystals, stretching out towards the positive pole, and presenting an appearance like that known as the tin-tree. The reduction is complete when hydrogen begins to escape at the negative pole. The crystalline metallic sponge may then be squeezed into a compact mass round the platinum terminal, well rinsed with water, removed from the platinum, and kneaded by the fingers into a solid lump. (Crookes.)

2. For reducing considerable quantities of thallium, it is best to employ metallic zinc. Plates of pure zinc (which should leave no residue whatever when dissolved in sulphuric acid) are arranged vertically round the sides of a deep porcelain dish holding a gallon. Crystallised sulphate of thallium, in quantities of about seven

pounds at a time, is then placed in the dish, and water poured over to cover the salt. Heat is applied, and, in the course of a few hours, the whole of the thallium will be reduced to the state of a metallic sponge, which readily separates from the plates of zinc on slight agitation. The liquid is poured off, the zinc removed, and the spongy thallium washed several times. It is then strongly compressed between the fingers, and preserved under water until it is ready for fusion. In this manner upwards of a hundredweight of metallic thallium may be reduced in the course of twenty-four hours. (Crookes.)

The metal is readily obtained in the coherent form by fusing the sponge. This is most conveniently performed under cyanide of potassium on the small scale, and under coal-gas when working with large quantities. In the former case, the sponge, strongly compressed and quite dry, is broken into small pieces, which are dropt one by one into cyanide of potassium fused in a porcelain crucible. They instantly melt, forming a brilliant metallic button at the bottom. When cold, the cyanide of potassium may be dissolved in water, when the thallium will be left in the form of an irregular lump, owing to its remaining liquid and contracting after the cyanide has solidified.

On the large scale, the fusion is best effected in an iron crucible. This is placed over a gas-burner, and a tube is arranged so that a constant stream of coal-gas may flow into the upper part of the crucible. Lumps of the compressed sponge are then introduced, one after the other as they melt, until the crucible is full of metal. It is then stirred up with an iron rod, and the thallium may either be poured into water and obtained in a granulated form, or cast into an ingot. Thirty or forty fusions have been performed in the same crucible without the iron being acted upon in the least by the melted thallium. (Crookes.)

According to Willm, pure thallium is best obtained by heating the oxalate in a glass tube, the metal then remaining in the fused state.

Properties.—Thallium is a perfect metal, with high metallic lustre. In colour it most resembles cadmium, not being so brilliantly white as silver, but free from the blue tinge of lead. The true colour can scarcely be seen by cutting or scraping the surface, as it tarnishes too quickly. It is best observed by scraping the metal under water, or by fusing it in hydrogen, and allowing the melted globule to flow away from the dross. When fused under coal-gas, the liquid metal in the crucible can hardly be distinguished from mercury. It takes a very high polish by friction with appropriate materials, under water. Thallium tarnishes at ordinary temperatures, quickly becoming coated with a film, which almost entirely protects it from further action of the air. The specific gravity of thallium varies according to the treatment it has undergone. A lump melted and slowly cooled under cyanide of potassium was found to have a density of 11·81, increasing by strong pressure to 11·88. When *squeezed* into wire, a portion was found to have a density as high as 11·91. Lamy gives it as 11·86. De la Rive states it to be 11·85 after fusion, and 11·80 after being *drawn* into wire. Thallium is the softest known metal admitting of free exposure to the air. The finger-nail, and even a piece of lead, scratch it readily. It marks paper like plumbago, forming a streak, blue at first, then turning yellow, and in a day or two fading nearly out. Sulphide of ammonium or sulphuretted hydrogen will at any time temporarily restore the dark streak. Thallium has less tenacity than lead, and does not become brittle at any temperature between − 18° C. (0° F.) and its melting-point. It is very malleable, and can be hammered into foil as thin as tissue-paper; its hardness is not sensibly increased by hammering. It can be drawn into wire only with difficulty, but it is squeezed into wire very readily, by the process technically known as "squirting." Thallium-wire is almost devoid of elasticity, retaining any form into which it is bent, with scarcely a tendency to spring to its original position. When first prepared, the wire appears amorphous, and will remain so if kept at the ordinary temperature in carbonic anhydride, or in petroleum free from air. In water it gradually becomes crystalline, resembling the *moiré* of tinplate; this effect is immediately produced when thallium in wire, ingot, or plate, tarnished or clean, is boiled in water.

Thallium is a very crystalline metal, and crackles almost as much as tin when bent. When several pounds of it are fused, and allowed to cool slowly, and the interior liquid portion poured off from that which has solidified, well-defined crystals, in octahedrons and fernlike forms, are produced. The melting-point of thallium is 290°, according to Lamy; 293·9° according to Crookes, who determined it by fusing about two pounds of the pure metal. Thallium does not become pasty before melting; it expands considerably before complete fusion, and contracts strongly on cooling. Two pieces of the metal weld together under strong pressure at the ordinary temperature, and after filling the steel die with scraps and cuttings, they may be readily squeezed into a solid rod, apparently as tenacious as when obtained by fusion.

The most characteristic property of thallium is the intense green colour which the metal or any of its compounds communicates to a colourless flame. This colour, when examined in the spectroscope, is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line, coinciding with the number 1442·6 on Kirchhoff's spectrum-chart. The thallium-spectrum is simpler than that of any other element yet examined. An amplifying power as great as has ever been applied to the spectrum (16 heavy glass prisms), does not affect the integrity of the line, and the high temperature of the hydrogen- or oxyhydrogen-flame shows no new lines; thallium has therefore a simpler spectrum than sodium or lithium, which stand next to it in this respect. The spectral reaction of thallium is very delicate, the 5-millionth part of a grain of thallium-sulphate being sufficient to produce it.

The length of the wave of the green thallium-line is 0·0005348 millimetre. (J. Müller, Pogg. Ann. cxviii. 641.)

When sparks from an induction-coil are passed between two pieces of thallium-wire, the light ceases to be purely monochromatic. On viewing it by the spectroscope, several new lines make their appearance; besides the usual intense line in the green, five others are particularly observable: first, a very faint one in the orange; next, two of nearly equal intensity in the green, more refrangible than Tl α, with a third much fainter, these three lines in the green being nearly equidistant; and, lastly, a bright well-defined line in the blue. The photographic spectrum contains several very characteristic groups of lines, recalling the features of the spectra of cadmium and zinc, and less strongly that of lead (W. A. Miller, Proc. Roy. Soc. xii. 407). The thallium-line has no counterpart in the black lines of the solar spectrum.

Thallium is strongly repelled by both poles of an electromagnet, being nearly equal to bismuth in diamagnetic character. In respect of electric conductivity, it lies between tin and lead. Taking the conducting power of silver at 100, that of thallium is 9·16 according to Matthiessen, 8·64 according to De la Rive. Matthiessen and Vogt find that the conducting power of thallium decreases, between 0° and 100°, by 31·420 per cent., which is a larger percentage decrement than that obtained for many other pure metals—namely, 25·307 per cent. The specific heat of thallium is given by Lamy at 0·0325, and by Regnault at 0·03349 and 0·03361.

Thallium, when heated in the air, begins to volatilise at a red heat, evolving brown vapours of oxide; it boils below a white heat, and may be distilled in a current of hydrogen. The hydrogen takes up mechanically a litle thallium, which is not deposited upon traversing five feet of cold glass tubing, as the emergent gas, when ignited, burns with a bright-green flame.

When heated to redness and plunged into oxygen, thallium burns brilliantly (Lamy). Before the blowpipe, on charcoal, it melts instantly, evolving copious brown fumes. The bead, if heated to redness, glows for some time after the source of heat is removed, continually evolving vapours which appear to be a mixture of metal and oxide. On cooling, the adjacent parts of the charcoal are found to be coated with small globules of volatilised metal, surrounded with a reddish amorphous sublimate of mixed protoxide and sesquioxide. The principal globule of metal is also coated with a fused layer of protoxide, resembling lead in this respect. When thallium is heated in an open glass tube, it melts, and becomes rapidly converted into the more fusible protoxide, which strongly attacks the glass. This oxide is of a dark-red colour when hot, solidifying to a brown crystalline mass.

Some of the compounds of thallium are very volatile, the chloride, for instance, distilling with the vapour of water, and volatilising when heated to a temperature below redness. Other compounds, such as the sulphate and phosphate, will bear a full red heat without loss.

Thallium is easily reduced to the metallic state. In aqueous solution, the metal is readily obtained by the electric current, or by the reducing action of metallic zinc. In the dry state, its salts may be reduced at a high temperature by charcoal and carbonate of sodium, or by cyanide of potassium, or from the chloride by an alkali-metal. The pure metal is scarcely attacked by hydrochloric acid, even when boiling. It is dissolved somewhat more readily by sulphuric acid, especially if it be in contact with a piece of platinum; nitric acid attacks it violently.

In electro-chemical position, thallium is very near cadmium, being precipitated from the sulphate by zinc and iron, but not by cadmium, tin, or copper.

Several thallium-salts are sensitive to light; the protochloride darkens readily, though by no means so rapidly as chloride of silver.

Thallium-salts are highly poisonous, producing symptoms like those of lead-poisoning. (Lamy, Compt. rend. lvii. 442; Jahresb. 1863, p. 265.)

Thallium forms two classes of compounds—namely, the thallious compounds, in which it is uni-equivalent; and the thallic compounds, in which it is tri-equivalent. Thus it forms two oxides, Tl^2O and Tl^2O^3, with corresponding chlorides, bromides, iodides, and oxygen-salts. In some of its chemical relations it resembles the alkali-metals, forming a readily soluble and highly alkaline protoxide, a soluble and alkaline carbonate, an insoluble chloroplatinate, and a thallio-aluminic sulphate, similar in form and composition to common potash-alum. In most respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting-point, specific heat, and electric conductivity. Its relationship to the heavy metals is further shown by its high atomic weight; the complexity of its photographic spectrum, which contrasts strongly with the simplicity of those of the alkali-metals (Miller); the highly poisonous character of its compounds; its easy reduction from solution by zinc; the production of a brown insoluble peroxide by electrolytic action (p. 753); the complete or nearly complete insolubility of its sulphide, phosphide, iodide, bromide, chloride, chromate, and phosphate. Thallium differs also essentially from the alkali-metals in the slight affinity of its protoxide for water, this oxide not only being non-deliquescent, but remaining in the anhydrous state when its aqueous solution is evaporated at ordinary temperatures in a vacuum over oil of vitriol. The argument in favour of its relationship to the alkali-metals, derived from the formation of a thallium-alum, can no longer be considered valid, now that a silver-alum of similar form and composition has been shown to exist (p. 580).

THALLIUM, ALLOYS OF. These compounds have not been much studied. When thallium is projected into a crucible containing melted copper, it boils, and in great part volatilises, some however uniting with the copper. By repeated additions of thallium, a hard, brittle, white alloy may be formed. With a still smaller quantity of thallium, the mixture is gold-coloured; and with 95 per cent. of copper, it forms a hard button, flattening somewhat under the hammer, but soon cracking at the edges. In small quantities, thallium appears to diminish the malleability and ductility of copper. Copper prepared in Spain, by the cementation-process already described, frequently contains considerable quantities of thallium, which may perhaps account for its pre-eminently bad quality.—With lead, thallium melts readily, forming a malleable alloy.—With mercury it unites easily, forming a solid crystalline amalgam.—Platinum and thallium unite, with incandescence. When a piece of metallic thallium is placed on a platinum-wire loop, and held in the flame of a spirit-lamp, the two metals rapidly melt together, becoming nearly white hot, and evolving abundant fumes of thallium; the resulting alloy is highly crystalline, very hard, and almost as brittle as glass. The most convenient way of obtaining the green light of thallium is to alloy a platinum-wire loop in this manner. When this loop is introduced into a spirit-lamp, or heated before the blowpipe, a green tint of extraordinary splendour is communicated to the flame.—An alloy of thallium and tin is easily obtained by fusion under cyanide of potassium, or coal-gas. With 5 per cent. of thallium, the alloy is perfectly malleable.

THALLIUM, BROMIDES OF. The *protobromide*, or *Thallious bromide*, $TlBr$, is formed by adding thallium to bromine, or by double decomposition. It forms a very pale-yellow precipitate, fusible below redness, and is intermediate in solubility between the chloride and iodide (Lamy). According to Willm (Bull. Soc. Chim. 1864, ii. 89), it is nearly insoluble in cold, and very slightly soluble in boiling water. In contact with bromine and a small quantity of water, it gradually dissolves, with rise of temperature, to a liquid, which, when evaporated in a vacuum, solidifies to a pungent, yellow, deliquescent, crystalline mass of impure *tribromide*, or *thallic bromide*, $TlBr^3$ (containing rather less bromine than that required by the formula). On mixing the aqueous solution of the tribromide with the protobromide, or subjecting it to partial reduction, the hot liquid yields long, siskin-yellow, shining needles, appearing under the microscope as quadratic prisms, and consisting of the *dibromide*, $Tl^2Br^4 = TlBr.TlBr^3$. They are decomposed by water into a protobromide which separates, a tribromide which remains dissolved, and a *sesquibromide*, $Tl^4Br^6 = TlBr^3.3TlBr$, which crystallises in translucent, orange-red, six-sided laminæ. This last compound is likewise decomposed by treatment with water, with separation of protobromide. (Willm.)

The tribromide forms, with *bromide of ammonium*, a double salt, $NH^4Br.TlBr^3.5H^2O$, crystallising in long, yellow, transparent needles, which easily give off their water in a vacuum. A concentrated alcoholic solution of the tribromide mixed with *ammonia*, yields a white precipitate of the compound $TlBr^3.3NH^3$, which quickly turns yellow, and is easily decomposed by water, with separation of black sesquioxide of thallium. (Willm.)

A compound of thallic bromide with ethylic oxide, $2TlBr^3.3(C^2H^5)^2O$, is produced by adding bromine to anhydrous ether in which metallic thallium or the protobromide is suspended. This compound dissolves in bromide of ammonium, yielding the double salt $NH^4Br^3.TlBr^3$, with 2 at. and 3 at. water, the former hydrate crystallising in rhomboïdal or six-sided tables, the second in needles; both melt in their water of crystallisation below 100°. (Nicklès, Compt. rend. lviii. 537.)

THALLIUM, CHLORIDES OF. Thallium forms four chlorides analogous to the bromides:—

Protochloride of Thallium, or *Thallious Chloride*, TlCl.—Metallic thallium is attacked at ordinary temperatures by chlorine; when heated in the gas, it burns and forms a yellow liquid, which solidifies on cooling to a pale-yellow or white crystalline mass. If excess of chlorine has been present, the product consists almost entirely of higher chlorides; but in presence of an excess of thallium, the white protochloride is the only compound formed. Boiling hydrochloric acid attacks thallium but slowly, the action soon ceasing, owing to the formation of a layer of difficultly soluble chloride of thallium. When hydrochloric acid, or a soluble chloride, is added to a solution of thallious oxide or a thallious salt, a white curdy precipitate of protochloride is thrown down, scarcely to be distinguished at first sight from chloride of silver. When boiled in water, it dissolves like chloride of lead, and separates again on cooling; the crystals, however, are much smaller and less brilliant than those of chloride of lead. Protochloride of thallium is also precipitated when sulphurous acid or an alkaline sulphite is added to one of the higher chlorides.

One part of the protochloride dissolves in 283·4 pts. of water at 15·5°, and in 52·5 pts. of boiling water. It is insoluble in alcohol, and scarcely, if at all, more soluble in aqueous ammonia, cyanide of potassium, or hydrochloric acid, than in water. When boiled in nitric or nitromuriatic acid, it is converted into a higher chloride. It may be heated to 260° without loss of weight; at a slight increase of heat, it suddenly melts to a thin brown liquid, white vapours being simultaneously evolved. On cooling, it solidifies to a white, shining, crystalline, somewhat flexible mass. The specific gravity of the fused chloride is 7·02 (Lamy). The fused lump is reduced to the metallic state by zinc and dilute acid, like fused chloride of silver. According to Lamy, chloride of thallium is unalterable by light; but according to Crookes, it undergoes a considerable darkening when exposed either to sunlight or diffused daylight.

Protochloride of thallium forms double salts with trichloride of gold and tetrachloride of platinum.—The *chloroaurate* separates from the hot aqueous solution containing a slight excess of auric chloride, in brilliant gold-coloured crystals; it is slightly soluble in water, and when ignited leaves an alloy of gold and thallium.—The *chloroplatinate*, $2TlCl.PtCl^4$, is precipitated as a pale-yellow crystalline powder, very sparingly soluble in water, much less so than the corresponding potassium-, rubidium-, or cæsium-salts (*q.v.*), 1 pt. of it requiring for solution 15,585 pts. water at 15·5°, and 1,948 pts. at 100°. (Crookes.)

Sesquichloride of Thallium, Tl^2Cl^3 or $Tl^4Cl^6 = TlCl^3.3TlCl$.—This compound is produced by dissolving thallium or the protochloride in nitromuriatic acid, and separates on cooling in yellow crystalline scales. It may also be prepared by heating the trichloride till it melts, and no longer gives off chlorine (p. 748). [Werther obtained by these processes only variable mixtures of the protochloride and trichloride; but other experimenters have obtained a definite product.] The sesquichloride, when heated, melts below redness, forming a dark-brown liquid, which solidifies to a lighter-coloured mass. It is soluble in 380·1 times its weight of water at 15·5°, and in 52·9 pts. of boiling water. Pure water produces a slight decomposition into sesquioxide and protochloride, which, however, may be prevented by the addition of a drop of nitric or hydrochloric acid. When slowly crystallised from slightly acidulated boiling water, it separates in brilliant orange-yellow hexagonal plates, considerably darker than when it is obtained by more rapid crystallisation, and presenting the closest resemblance to iodide of lead. Sesquichloride of thallium is also precipitated by the cautious addition of sulphite of sodium to one of the higher chlorides. Whenever it separates from a liquid, it shows remarkable crystalline characters, and when just precipitated, produces a magnificent satiny lustre in the liquid. Solution of ammonia, potash, or even thallious oxide, added to the sesquichloride, produces instant decomposition into sesquioxide and protochloride, according to the following equation:

$$4Tl^2Cl^3 + 3(NH^4)^2O = Tl^2O^3 + 6TlCl + 6NH^4Cl.$$

When pure dry ammoniacal gas is passed over the sesquichloride, heat being applied with a spirit-lamp, the salt first assumes a deep orange tint, without fusing, and loses its brilliant, almost metallic lustre. On increasing the heat, the chloride fuses, and at the same time sal-ammoniac vapours are abundantly evolved. The melted compound froths up, and assumes a deeper tint, ultimately becoming brown, and then gradually paler, until there finally remains perfectly white protochloride of thallium.

The reaction between ammonia-gas and sesquichloride of thallium is represented by the following equation:—

$$3Tl^2Cl^3 + 4NH^3 = 6TlCl + 3NH^4Cl + N.$$

The sesquichloride, heated in a stream of *sulphydric acid gas*, is converted into black sulphide of thallium, with evolution of hydrochloric acid and volatilisation of sulphur. Its aqueous solution yields, with sulphydric acid, a slight red precipitate, which disappears on boiling, leaving only a small quantity of sulphur.—*Sulphide of ammonium* or *potassium* produces complete precipitation. (Hebberling, Jahresb. 1865, p. 250.)

Platinic chloride added to the aqueous solution throws down thallious chloroplatinate, $2TlCl.PtCl^4$, while thallic chloride remains in solution. (**Werther**, *ibid.* p. 246.)

Dichloride of Thallium, $Tl^2Cl^4 = TlCl^3.TlCl$, is formed by carefully heating either thallium or the protochloride in a slow current of chlorine, the resulting chloride being kept liquid. The dichloride is pale-yellow, rather hygrometric, and decidedly more fusible than the sesquichloride. It is reduced to sesquichloride by heat. (Lamy.)

Trichloride of Thallium, or *Thallic Chloride*, $TlCl^3$.—This compound is formed by dissolving the trioxide in hydrochloric acid, or by acting upon thallium or a lower chloride with a large excess of chlorine at a gentle heat. According to Werther (Jahresb. 1864, p. 247), it is most easily prepared by treating thallium or the protochloride with chlorine-gas under water, till the resulting solution is no longer precipitated by platinic chloride. The solution freed from excess of chlorine by a stream of carbonic anhydride, and evaporated in a vacuum, yields a crystalline mass composed of long colourless prisms of the hydrated trichloride, $TlCl^3.H^2O$, sometimes also long deliquescent needles, containing $2TlCl^3.15H^2O$. It melts easily, and decomposes with loss of chlorine, the residue consisting, according to **Lamy**, of the sesquichloride; according to **Werther**, of mixtures of the trichloride and protochloride.

Trichloride of thallium unites with the chlorides of the alkali-metals, forming colourless crystallisable double salts, which easily decompose with separation of thallic oxide (Ficklès, J. Pharm. [4], i. 26).—The *ammonium-salt*, $3NH^4Cl.TlCl^3.2H^2O$, is produced (with simultaneous formation of chloride of nitrogen) by passing chlorine into a solution of thallious chloride containing a large quantity of sal-ammoniac; more readily by digesting the ether-compound of thallic chloride (*infra*) with sal-ammoniac; it then separates in large six-sided tables, belonging to the trimetric system, easily soluble in water and in alcohol (Nicklès).—The *potassium-salt*, $3KCl.TlCl.\frac{3}{2}H^2O$, crystallises from a mixed solution of the component chlorides in modified cubes (Willm).—The *cupric salt*, $Cu''Cl^2.2TlCl^3$, separates from the mixed solution of its constituent salts, in opaque green crystals, simultaneously with colourless transparent prisms, which have not been examined. (Willm.)

A compound of thallic chloride with *ethylic oxide*, $TlCl^3.(C^2H^5)^2O.HCl + H^2O$, is obtained, according to Nicklès (Jahresb. 1864, p. 252), by passing chlorine into anhydrous ether, in which metallic thallium or the protochloride is suspended. Two layers of liquid are then formed, the lower containing the ether-compound, which remains behind on evaporating the product at 100° in a stream of carbonic anhydride. It dissolves in ether and in water containing hydrochloric acid, decomposes alkaline carbonates, and when treated with an excess of the latter, deposits sesquioxide of thallium. With sulphurous acid it yields protochloride of thallium.

THALLIUM, CYANIDE OF. Obtained by mixing the concentrated solutions of potassic cyanide and thallious carbonate, or by neutralising thallious oxide with prussic acid (Kuhlmann); more easily by mixing strong solutions of potassic cyanide and thallious nitrate (Crookes). It separates in shining crystalline plates, not very soluble in water. When heated, it decrepitates and melts easily, and when intensely heated on platinum-foil, volatilises without reduction, or alloying with the platinum.

Ferroso-thallious Cyanide, or *Ferrocyanide of Thallium*, precipitated on mixing ferrocyanide of potassium with thallious nitrate, forms yellow crystals, slightly soluble in water.

THALLIUM, DETECTION AND ESTIMATION OF. 1. *Reactions in the Dry Way.*—The behaviour of metallic thallium before the blowpipe, and the peculiar characters of its spectrum, have been already described (p. 745). The green line Tlα is alone sufficient to distinguish thallium from all other elements. Thallium-salts, when ignited, generally fuse below redness, and then volatilise; some of them, however, as the sulphate and phosphate, will stand a bright-red heat without change; the chlorides, on the other hand, distil over with vapour of water. On charcoal before the blowpipe they volatilise, communicating an intense green colour to the flame.

2. *Reactions in Solution.*—*a.* Thallious salts are for the most part colourless,

unless the acid itself is coloured. They are mostly soluble in water, neutral to test-paper, and have a slight metallic taste. Their aqueous solution is rapidly precipitated in metallic crystals by *zinc*, and slowly by *iron*.—*Phosphoretted hydrogen* precipitates a black phosphide.—*Sulphydric acid* added to a solution of a thallious salt containing a weak acid, such as carbonic or acetic, separates the whole of the metal in the form of a deep brown sulphide; from solutions of thallium-salts of the stronger acids, such as the sulphate or nitrate, sulphydric acid precipitates nothing if the acid is in excess, and only a small portion of the metal if the solution is neutral.—*Sulphide of ammonium* precipitates thallium-salts completely, the precipitated sulphide being insoluble in sulphide of ammonium, in caustic alkalis, their carbonates and cyanides, and only slightly soluble in acetic acid.—*Hydrochloric acid* and *soluble chlorides* precipitate a difficultly soluble white chloride; *hydrobromic acid* and *bromides* precipitate a white nearly insoluble bromide; and *hydriodic acid* and *iodides* precipitate an insoluble yellow iodide.—*Alkalis, alkaline carbonates*, or *bicarbonates* produce no change in thallious salts; *phosphate of sodium* gives a white precipitate, nearly insoluble in ammonia, easily soluble in acids.—*Chromate of potassium* gives a yellow precipitate of thallious chromate, insoluble in cold nitric or sulphuric acid, but turning orange-red on boiling in the acid solution.—*Platinic chloride* precipitates a very pale-yellow insoluble double salt.

From these reactions it appears that, in examining a mixed metallic solution, according to the ordinary method of qualitative analysis (i. 217), thallium will be found in the precipitate thrown down by sulphide of ammonium, together with iron, nickel, manganese, &c. From these metals it may be easily separated by precipitation with iodide of potassium or platinic chloride, or by reduction to the metallic state with zinc. According to Hebberling, iodide of potassium is, next to the spectral reactions, the most delicate of all tests for the presence of thallium, producing a visible precipitate in a solution of thallious sulphate, containing only 0·0105 pt. of the salt in 1,000 pts. of the liquid.

β. Thallic salts are easily distinguished from thallious salts by their behaviour with alkalis, and with soluble chlorides or bromides. Their solutions give with *ammonia*, and with fixed *alkalis* and their *carbonates*, a brown gelatinous precipitate of thallic oxide, containing the whole of the thallium. *Hydrochloric acid* and soluble *chlorides* or *bromides* produce no precipitate in solutions of pure thallic salts; but if a thallious salt is likewise present, a precipitate of sesquichloride or sesquibromide is formed. Oxalic acid forms in solutions of thallic salts a white pulverulent precipitate, *phosphoric acid* a white gelatinous precipitate, and *arsenic acid* a yellow gelatinous precipitate: these three precipitates, however, are sparingly soluble only in presence of a large quantity of free acid, so that they are not always produced by the corresponding alkaline salts.—*Sulphocyanate of potassium* forms in acid solutions of thallic salts a black-grey precipitate, in very slightly acid solutions a yellow precipitate, which is dissolved by boiling water, and at the same time reduced to a thallious salt.—*Chromate of potassium* does not precipitate thallic salts (Willm, Jahresb. 1865, p. 255). According to Strecker, on the contrary (*ibid.* p. 253), chromate of potassium forms, in a solution of thallic sulphate, a yellow precipitate, which turns brown in contact with water. Thallic nitrate gives with *ferrocyanide of potassium* a siskin-green, with the *ferrocyanide* a yellow precipitate. A solution of thallic sulphate or nitrate, mixed with *tartrate of sodium*, gives, with *ammonia*, a white curdy precipitate, soluble in excess of ammonia, to a liquid which deposits the brown sesquioxide on boiling. But when the sesquioxide is boiled with tartaric acid, carbonic anhydride and formic acid are evolved, and a solution is formed, which deposits crystals of thallious tartrate. The ammoniacal solution of thallic oxide formed in presence of tartaric (or phosphoric) acid, gives with *sulphide of ammonium* or *sulphydric acid*, a brown precipitate, melting at the boiling heat to a metallically lustrous ball, which dissolves in hot dilute sulphuric acid, with evolution of sulphydric acid and deposition of sulphur.—*Iodide of potassium* added to the same ammoniacal solution, forms a black precipitate, which changes on boiling to thallious iodide mixed with a small quantity of iodoform. (Strecker.)

3. *Estimation and Separation.*—Thallium, when it occurs in solution as a thallious salt, is most conveniently estimated as protoiodide, TlI, in which state it is obtained by precipitation with iodide of potassium. The precipitate is quite permanent in the air, and at the temperature at which it is weighed. It is but very slightly soluble in water, insoluble or nearly so in saline solutions, alcohol of 92 per cent., and aqueous ammonia, but perceptibly soluble in water containing free acids or fixed alkalis. On mixing the hot ammoniacal solution of a thallious salt with iodide of potassium, the thallious iodide separates immediately as a curdy precipitate, which, after standing for several hours, may be collected on a weighed filter, and washed with

alcohol, or, if this is inadmissible, with ammonia. It is then dried at 115°, and weighed: it contains 49·40 per cent. thallium. (G. Werther, Zeitschr. Anal. Chem. iii. 1; Jahresb. 1864, p. 712.)

Thallium may also be estimated in the form of thallious sulphate, but not quite so exactly as by the method just described. The sulphate bears a dull red heat without perceptible volatilisation, but it is volatilised at a bright-red heat. Thallium is very completely precipitated from solutions of thallium-salts by *platinic chloride*; but the precipitated chloroplatinate is troublesome to manage, as it is very finely divided, and is apt to run through the filter when washed with water or with alcohol. (Werther.)

In solutions of thallic salts, the thallium may be estimated by reducing the thallic to thallious salts with an alkaline sulphite, and then precipitating with *iodide of potassium* (Crookes), or, by precipitating the thallium with *ammonia*, as sesquioxide, and collecting the precipitate on a weighed filter. The separation of thallious from thallic salts may be effected—at least in the case of the chlorides or sulphates,—by first precipitating the sesquioxide with ammonia, and then throwing down the remaining portion of thallium from the hot dilute filtrate by iodide of potassium (Werther). The separation may also be effected by platinic chloride, which precipitates only the thallious salt.

The method of precipitation with iodide of potassium serves also to separate thallium from most other metals, the solution being first mixed with an alkaline sulphite to ensure the reduction of any thallic salt that may be present to the state of thallious salt. If copper is present, the iodide of potassium will throw down cuprous as well as thallious iodide; but by treating the washed precipitate with ammonia, in contact with the air, the copper will be dissolved out, and the thallium will remain as thallious iodide. The separation of copper from thallium may also be effected, though not so exactly, by precipitating the copper with sulphuretted hydrogen in an acid solution. The same method serves also to separate thallium from lead and silver. The precipitated sulphides are apt, however, to carry down small quantities of thallium-sulphide.

Small quantities of thallium often occur in bismuth minerals and preparations made from them, especially the carbonate. To detect the thallium, the dilute solution of the substance is mixed with a slight excess of sodium-carbonate, and a small quantity of potassium-cyanide, then gently warmed and filtered. If the bismuth-compound contained only 1 pt. of thallium in 100,000, the addition of a few drops of ammonium-sulphide will produce a dark-brown precipitate of thallium-sulphide, which gradually collects together, and may be further examined by the spectroscopic method. From carbonate of bismuth, thallium may be easily dissolved out by digestion with cyanide of potassium, less completely with carbonate of sodium. (Crookes.)

Volumetric Estimation.—Thallium may be estimated volumetrically with *permanganate of potassium* in the same manner as iron. For this purpose it must be in the state of thallious chloride, or of a thallious oxygen-salt mixed with hydrochloric acid, and the solution must not contain more than 1 gramme of thallium in 500 c.c.; the permanganate-solution should also be more dilute than for the estimation of iron. The titration of the permanganate may be made with pure iron, with thallium, or with a thallious salt (the alum, for example); 2 at. iron (112 pts.), correspond to 1 at. thallium (204 pts.), inasmuch as the protochloride TlCl is converted by oxidation into the trichloride $TlCl^3$, so that 1 at. thallium takes up the same quantity of oxygen as 2 at. iron. The solution of the thallious salt, diluted as above mentioned, is mixed with a few drops of hydrochloric and a few drops of sulphurous acid, and heated to the boiling-point to expel the latter; then left to cool, and mixed with the permanganate. (Willm, Zeitschr. Ch. Pharm. 1863, p. 479; Jahresb. 1863, p. 689.)

4. *Atomic Weight of Thallium.*—Lamy, by decomposing the sulphate with nitrate of barium, and the chloride with nitrate of silver, obtained numbers varying between 203·5 and 204·6; mean, 204·2. Crookes found, as a mean of five experiments, the number 202·96. Werther also estimates it at somewhat lower than 204, namely, about 203·5 or 203·7. The number 204 is, however, generally adopted.

THALLIUM, FLUORIDES OF. Thallium forms two fluorides, TlF and TlF^3.—Metallic thallium is but slowly attacked by hydrofluoric acid. The carbonate, however, dissolves easily in the acid, and the solution deposits *thallious fluoride*, in white hydrated crystals derived from an oblique rhombic prism, with adamantine facets; they are not altered by light. On heating these crystals, the anhydrous fluoride, TlF, volatilises as a white, crystalline, anhydrous mass, which blackens like chloride of silver on exposure to light. Thallium-fluoride forms an acid solution, even after repeated crystallisation. The crystallised compound decomposes slowly on exposure to the air, giving off hydrofluoric acid (Fr. Kuhlmann, Bull. Soc. Chim. [1864],

i. 57; Jahresb. 1864, p. 253). Willm (Jahresb. 1865, p. 244), by dissolving carbonate of thallium in aqueous hydrofluoric acid, and evaporating, obtained thallious fluoride, in hydrated, very deliquescent, six-sided tables, which gave off their water at 100°, with partial decomposition. According to M. Buchner (J. pr. Chem. xlvi. 404), thallious fluoride separates from its solution, by slow evaporation, in colourless cubo-octahedrons, having a strong vitreous lustre. It dissolves, with alkaline reaction, in 1·25 pt. water at 15°, more easily in boiling water, sparingly in alcohol. When heated, it melts, volatilises, and solidifies again in the crystalline form. A solution containing excess of hydrofluoric acid deposits, by evaporation over oil of vitriol, *hydrothallious fluoride*, $HF.TlF$, in crystals having the same form as those of thallious fluoride. This compound has an acid reaction, dissolves in an equal weight of water, and decomposes above 100° into hydrofluoric acid and fluoride of thallium (Buchner). Kuhlmann, by treating carbonate of thallium with silicofluoric acid, obtained a *silicofluoride of thallium*, $2TlF.SiF^4.2H^2O$. It crystallises in cubic forms, dissolves easily in water, forming an acid solution, distils without decomposition, and attacks glass after some time only. Werther, by treating carbonate of thallium with hydrofluoric acid containing a large quantity of silica, obtained the anhydrous silicofluoride, $2TlF.SiF^4$, in regular octahedrons, distorted so as to resemble hexagonal prisms.

Thallic Fluoride, TlF^3, is obtained, by the action of strong hydrofluoric acid on thallic oxide, as a dark-green precipitate, insoluble in water and in cold hydrochloric acid. When heated, it turns brown, melts, and, at a higher temperature, volatilises, probably as thallious fluoride. (Willm.)

THALLIUM, IODIDES OF. The *protoiodide*, or *Thallious iodide*, TlI, is formed by direct combination of its elements, or by double decomposition. It forms a beautiful yellow powder, rather darker than sulphur, and melting, below redness, to a scarlet liquid, which, as the mass cools, remains scarlet for some time after solidification, then changes to bright-yellow. The dried precipitate, when spread on paper with a little gum-water, undergoes a similar but opposite change to that experienced by mercuric iodide when heated, the yellow surface when held over a flame suddenly becoming scarlet, and frequently remaining so for several days after cooling; hard friction with a glass rod, however, changes the scarlet colour back to yellow (Crookes). According to Werther, thallious iodide precipitated from dilute solutions, is lemon-yellow; but when precipitated from hot concentrated solutions, it is orange-yellow at first, and afterwards becomes lemon-yellow. When precipitated from a hot solution of thallious acetate, it retains its orange-yellow colour, and forms anhydrous microscopic cubes, or cubo-octahedrons, which, when heated, melt to a black liquid, and partially sublime. Thallious iodide is very sparingly soluble in water, requiring, according to Crookes, 4,453 pts. of water at 17·2°, and 842·4 pts. at 100°, to dissolve it; according to Hebberling, 1 pt. of it dissolves in 11,676 pts. of water at 16° to 17°, in 864 pts. at 100°, and in 18,934 pts. of 98 per cent. alcohol at 19°; according to Werther, in 20,000 pts. water at 13·5°, in 10,000 pts. at 23·4°, in 5,400 pts. at 45°, and 56,330 pts. of 85 per cent. alcohol at 13·5. According to Crookes, it is somewhat more soluble in aqueous iodide of potassium than in pure water; according to Hebberling, on the contrary, it is less soluble in saline solutions, especially in iodide of potassium, than in pure water.

Thallic Iodide, TlI^3.—By the action of iodine on thallium and ether, a brown solution is formed, which gradually deposits crystals of thallic iodide, easily soluble in ether containing iodine. They are rhombic prisms, exhibiting the combination $\infty P . \infty\bar{P}\infty . \bar{P}\infty . n\bar{P}\infty$. Angle $\infty P : \infty P$ (macr.) = 79° 45′; $\infty P : \infty\bar{P}\infty$ = 140° 38′; $\bar{P}\infty : \infty\bar{P}\infty$ = 160° 35′. (Nicklès.)

Ammonio-thallic iodide, $3NH^4I.TlI^3$, forms red rhombic plates, which, when heated, give off water and iodine without melting. (Nicklès.)

When 1 at. thallious iodide is treated with a solution of 2 at. iodine, in alcoholic iodide of potassium, the liquid deposits, on evaporation, large crystals of *potassio-thallic iodide*, $KI.TlI^3$, which are black by reflected, garnet-red by transmitted light, and yield a bright-red powder. This compound is resolved at 56°—60°, and more completely at 100°, into iodide of potassium, thallious iodide, and free iodine; it is also decomposed by water. (Willm, Jahresb. 1864, p. 251.)

THALLIUM, OXIDES OF. Thallium forms two oxides—namely, a protoxide, Tl^2O, and a sesquioxide, Tl^2O^3. It oxidises in the air almost as rapidly as an alkali-metal, the surface soon becoming covered with a thin film of oxide, which protects the metal from further oxidation. The superficial tarnish consists of the protoxide containing a minute quantity of the sesquioxide. If the metal has been oxidised at 100° rather more sesquioxide is formed, and at the melting-point of the metal, the protoxide which forms is mixed with a large quantity of sesquioxide. Thallium, when melted, behaves like lead, the oxide fusing like litharge; the fused oxide is absorbed by bone-ash, and a silver-thallium alloy can be cupelled like silver-lead. Thallium does not decompose pure water, either at the common temperature, or when boiling; but at a red heat the vapour of water is decomposed by thallium, with formation of oxide and separation of hydrogen, which burns with a green flame. Alcohol appears to be decomposed by the metal more readily than water.

(Respecting Schönbein's observations on the reactions of thallium with ordinary oxygen, ozone, and hydric peroxide, see J. pr. Chem. xciii. 35; Bull. Soc. Chim. 1864, i. 180; Jahresb. 1864, p. 170.)

Protoxide of Thallium, or *Thallious Oxide*, Tl^2O.—This oxide may be prepared by allowing granulated thallium to oxidise in warm moist air, and then boiling in distilled water. By repeating this operation two or three times, a saturated hot solution of the oxide is formed. Upon filtering, the small quantity of carbonate which may have formed separates at first in white needles, whilst, upon further cooling, the hydrated oxide crystallises out in yellow needles.

Anhydrous protoxide of thallium is formed by exposing these yellow crystals in a vacuum over sulphuric acid; it then forms a reddish-black mass, retaining the shape of the crystals. When heated to about the melting-point of the metal, it melts to a brown limpid liquid, which, at a higher temperature, evolves reddish-brown vapours, partially oxidising at the same time to the sesquioxide. On cooling, the brown liquid solidifies to an almost black crystalline mass. The fused oxide attacks glass and porcelain, removing the silica. Protoxide of thallium is decomposed by hydrogen at a red heat, forming water and metallic thallium. The decomposition, however, is never perfect, because the oxide melts and volatilises. When fused with sulphur, it forms sulphide of thallium, and in aqueous solution it is reduced to the metallic state by zinc, or by the electric current.

Hydrated Oxide of Thallium, or *Thallious Hydrate*, $Tl^2O.H^2O$ or $TlHO$, is prepared as above described, or it may be obtained, as recommended by Lamy, by decomposing a solution of the sulphate with baryta-water, and evaporating the alkaline solution in a vacuum. This method, however, is somewhat tedious, and there is great difficulty in getting the oxide free from baryta. The best method of obtaining perfectly pure thallious hydrate, is to add water to the oily compound of oxide of thallium and alcohol (p. 757). This at once separates the hydrate in the form of a bright-yellow crystalline mass, which may be separated from water and alcohol by exposure to warm dry air.

Thallious hydrate forms pale-yellow, long, prismatic crystals, which lose water, and become almost black and anhydrous by exposure to the temperature of a water-bath in air, or over sulphuric acid in a vacuum at the common temperature. On the addition of water, the dark oxide immediately becomes hydrated and yellow. It has a slight tendency to absorb oxygen, and after evaporation and re-solution, it always leaves a slight residue of sesquioxide.

Willm, by a method which he does not describe, once obtained thallious hydrate in rather large rhombic crystals, containing $TlHO.H^2O$.

Aqueous Solution.—Protoxide of thallium is a powerful base, dissolving readily in water, and forming a colourless strongly alkaline solution. It has a slight odour, similar to that of potash, dissolves the skin and feels greasy, acts strongly on the hair and nails, staining them a deep and very permanent brown colour. It blues litmus-paper, browns turmeric-paper, has a metallic alkaline taste, and neutralises acids perfectly. It eliminates ammonia from chloride of ammonium, and reacts with hydrochloric acid, iodide of potassium, sulphide of ammonium, &c., in the characteristic manner of a thallium-salt. An aqueous solution of thallious oxide has a greater similarity to potash than to ammonia in its reactions with metallic salts. When added to solutions of salts of magnesium, cerium, manganese, zinc, cadmium, lead, iron (ferrous or ferric), cobalt, nickel, copper, mercury, or silver, or to thallic salts, it precipitates the respective oxides, without redissolving them in excess. From salts of aluminium and chromium it precipitates the hydrated oxides, and easily redissolves them when in excess, forming with alumina a solution which is not altered by boiling, but is precipitated by a current of carbonic anhydride; and with chromium a green solution precipitated on boiling.

Sesquioxide of Thallium, or *Thallic Oxide*, Tl^2O^3. *Peroxide of Thallium.*—This oxide is always formed when metallic thallium is heated, or even when a solution of the protoxide is evaporated in the air. When the metal is burnt in oxygen, the product is chiefly sesquioxide. This oxide is best prepared by adding potash, ammonia (or even protoxide of thallium) to a solution of a thallic salt, and drying the washed precipitate at about 260°. It is also formed when a voltaic current from two cells of Grove's batteries is passed through a solution of thallious sulphate, platinum terminals being used. If the solution is perfectly neutral, thallium slowly makes its appearance at the negative pole, whilst the positive pole becomes coated with a film, presenting at first the most brilliant colours of thin plates, and gradually increasing in thickness until it becomes a cake of thallic oxide. As the sulphuric acid accumulates in the liquid, the thallic oxide at first formed gradually dissolves. If the solution of thallious sulphate is rendered alkaline by ammonia, the thallic oxide is formed in larger quantity, scaling off and falling to the bottom of the liquid. (Crookes.)

Thallic oxide is also precipitated in the anhydrous state, on adding sodic hypochlorite to a solution of thallious chloride in sodic carbonate. (Strecker.)

Anhydrous thallic oxide is a dark-brown powder, fusing with difficulty, and evolving oxygen at a red heat, whereby it is reduced to thallious oxide. It is neutral to test-paper, insoluble in water and in alkalis, but dissolves readily in acids, forming hypometric and unstable salts, from the solutions of which the sesquioxide is completely precipitated by alkalis. According to Werther, the sesquioxide is partially reduced to protoxide in drying.

Thallic hydrate, $Tl^2O^3.H^2O = Tl'''HO^2$, is obtained by drying the precipitated sesquioxide at 100°. It forms a brown powder, a shade lighter than the anhydrous oxide. Deoxidising agents, such as sulphurous or oxalic acid, convert it into a thallious salt; partial reduction also takes place on evaporating its solution in hydrochloric acid. (Werther.)

THALLIUM, OXYGEN-SALTS OF. Both the oxides of thallium dissolve readily in acids, forming definite crystallisable salts, soluble in water; there are also a few insoluble thallium-salts, which are obtained by double decomposition. The general characters, both of the thallious and of the thallic salts, have been already described (p. 749).

a. Thallious Salts.

ACETATE, $C^2H^3TlO^2$.—This salt is obtained, in white silky needles, by dissolving thallious carbonate in a slight excess of strong acetic acid, evaporating, fusing the residue, dissolving it in water, and again evaporating. It begins to decompose at 171°, dissolves easily in water and in alcohol, and deliquesces in moist air. From its solution, the thallium is immediately and completely precipitated by sulphydric acid (Crookes). It crystallises from alcohol in silky needles. (Kuhlmann.)

ARSENATES.—*Dihydro-thallious arsenate*, TlH^2AsO^4, is obtained by boiling thallic oxide with arsenious acid and water, and crystallises from the concentrated solution in hard shining needles, unalterable at 150°. It dissolves readily in water, and the solution, on addition of ammonia, solidifies to a magma of slender crystals, consisting of the *trithallious salt*, Tl^3AsO^4. (Willm.)

BENZOATE.—Crystallises in pearly plates, and is not volatile. (Kuhlmann.)

BORATE.—Boric acid added to a solution of thallious carbonate, or borax added to the sulphate, throws down a white granular precipitate of thallious borate, insoluble in an excess of the precipitant, and in cold dilute sulphuric acid; soluble in boiling water.

BROMATE, $TlBrO^3$.—Resembles the iodate.

CARBONATE, Tl^2CO^3.—The film of oxide which forms upon the surface of metallic thallium, when exposed to the air, gradually absorbs carbonic acid, and becomes converted into carbonate, which frequently appears in the form of crystalline needles. A saturated aqueous solution of thallious oxide absorbs carbonic acid rapidly, and deposits the carbonate in crystals. Thallious carbonate may be prepared in quantity by allowing granulated thallium, slightly moistened with water, to oxidise in a warm atmosphere. Upon boiling out with water containing an excess of ammonium-carbonate, and filtering, thallious carbonate is deposited, as the solution cools, in yellowish crystals which may be rendered colourless by recrystallisation.

Thallious carbonate crystallises in groups of prisms, exhibiting faces comprised in one zone, and apparently belonging to the trimetric system. Observed faces $\infty\breve{P}\infty$, ∞P, $\infty\breve{P}2$, $\infty\bar{P}2$. Angle $\infty\breve{P}\infty : \infty P = 128° 32'$; $\infty\breve{P}\infty : \infty\breve{P}2 = 147° 53'$; $\infty\breve{P}\infty : \infty\bar{P}2 = 111° 3'$; $\infty P : \infty P = 102° 56'$. The crystals appear to be twins with the combination-face ∞P; they cleave parallel to the same face (W. H. Miller, Proc. Roy. Soc. xiv. 555).—The crystals are brilliant, highly refractive, and very heavy, resembling those of a lead-salt. The salt is anhydrous; its taste is mildly caustic and somewhat metallic, remaining on the tongue for a considerable time. When heated, it melts much below redness to a clear liquid, which solidifies to a dark-grey crystalline mass. It may be kept fused for a considerable time without decomposition or loss of weight, but, when heated to dull redness, evolves white vapours and bubbles of gas. The specific gravity of the fused salt is 7·06 (Lamy). It is not very soluble in cold water; 100 pts. of water dissolve 4·02 pts. at 15·5°, 11·7 pts. at 60°, and 27·21 pts. at the boiling-point. The specific gravity of a cold saturated solution is 1·0377 (Crookes). The solution has a slightly caustic, metallic taste and alkaline reaction, which is not completely removed by supersaturation with carbonic acid. (Crookes; compare Werther, Jahresb. 1864, p. 249.)

CHLORATE, $TlClO^3$.—Prepared by dissolving thallium in chloric acid, or by mixing the saturated solutions of potassium-chlorate and thallious nitrate. It is sparingly soluble in water, and crystallises in long anhydrous needles. Its solution, when heated, turns yellow, and gives off oxygen-compounds of chlorine; and the liquid, evaporated to a syrup, deposits small, brilliant, colourless crystals, which are instantly decomposed by water, alcohol, or ammonia, with formation of brown thallic oxide. (Crookes.)

CHROMATES.—The *neutral salt*, $TlCrO^2$ or $Tl^2O.Cr^2O^3$, is a pale-yellow precipitate, obtained by adding yellow chromate of potassium to a neutral solution of a thallious salt, rendered slightly alkaline by ammonia. It is very sparingly soluble in water.—The *dichromate*, $Tl^2O.2Cr^2O^3 = 2TlCrO^2.Cr^2O^3$, is obtained as an orange-yellow precipitate, on adding dichromate of potassium to a neutral thallious salt (Crookes). According to Willm, it is deposited, in microscopic orange-yellow crystals, from a solution of the neutral salt in boiling dilute sulphuric acid.

By boiling either of the preceding salts with moderately strong nitric acid, a solution is obtained, which on cooling deposits cinnabar-coloured crystals, probably consisting of the *trichromate*, $Tl^2O.3Cr^2O^3$, or $TlCrO^2.Cr^2O^3$. They are very sparingly soluble in water, 100 pts. of water dissolving only 0·0354 pts. at 15·5°, and 0·2279 pts. at 100° (Crookes).—A *sesquichromate*, $2Tl^2O.3Cr^2O^3$ or $4TlCrO^2.Cr^2O^3$, separates from a solution of the neutral salt in moderately concentrated sulphuric acid. (Willm.)

All the chromates of thallium are decomposed by strong hydrochloric acid, with evolution of chlorine, and formation of soluble chromic and thallious chlorides: on treating them with hydrochloric acid and alcohol, the whole of the thallium is separated as insoluble protochloride, while chromic chloride passes into the solution. Sulphate of sodium likewise separates the whole of the thallium as protochloride. (Crookes.)

CITRATE, $C^6H^5Tl^3O^7$.—Very deliquescent; crystallises with difficulty; soluble in alcohol. (Kuhlmann.)

CYANATE.—Precipitated on mixing the alcoholic solutions of potassium-cyanate and thallious acetate, in small brilliant plates, very soluble in water, slightly soluble in alcohol. (Kuhlmann.)

FORMATE, $CHTlO^2$.—Prepared by dissolving the carbonate in formic acid. It is very soluble in water, and melts, without decomposition, below 100°. (Kuhlmann.)

HYPOSULPHATE or DITHIONATE, $Tl^2S^2O^6$.—Very soluble in water, from which it separates in vitreous tabular crystals, probably isomorphous with the corresponding potassium-salt. (Werther.)

HYPOSULPHITE.—*Sodio-thallious hyposulphite*, $3Na^2S^2O^3.2Tl^2S^2O^3$, obtained by dissolving thallious chloride in a boiling solution of sodic hyposulphite, crystallises in long, silky, interlaced needles, containing 10 at. water; or from a small quantity of water in small grains, the quantity of crystallisation-water in which has not been determined. At a red heat it is resolved into sulphide and sulphate of sodium, and fused, brightly glowing sulphide of thallium. (Werther.)

IODATE, $TlIO^3$.—Precipitated, on mixing iodide of potassium with nitrate of thallium, as a white powder, slightly soluble in cold, more easily in warm water. (Oettinger.)

MALATE.—Deliquescent; crystallises with difficulty; melts below 100°. (Kuhlmann.)

MOLYBDATE, $TlMoO^2$, or $Tl^2O.Mo^2O^3$.—Obtained by double decomposition with molybdate of sodium and nitrate of thallium, and separates in nacreous scales, which dissolve sparingly in pure, easily in ammoniacal water. (Oettinger, Zeitschr. Ch. Pharm. 1864, p. 440.)

NITRATE, $TlNO^3$.—Crystallises from a solution of thallium in nitric acid, in dull white needles, which melt at 205°, with separation of a small quantity of thallic oxide. The salt thus purified gives no precipitate with ammonia. It has a specific gravity of 5·8, is insoluble in alcohol, but soluble in water, the saturated solution containing 9·7 per cent. of the salt at 18°, 43·7 per cent. at 58°, and 55 per cent. at 100° (Crookes). The crystals are trimetric, exhibiting the several combinations $\infty\breve{P}\infty . P$; $\infty P . P . 2\breve{P}2$; $\infty\breve{P}\infty . \bar{P}\infty . P . 2\breve{P}2$; $\infty\bar{P}\infty . \infty P . \infty\breve{P}2 . P . 2\breve{P}2$; $\infty\breve{P}\infty . \bar{P}\infty . \infty P . \infty\breve{P}2 . P . 2\breve{P}2$. Angle $\infty\breve{P}\infty : \bar{P}\infty = 141° 51·9'$; $\infty\breve{P}\infty : \infty P = 117° 3·7'$; $\bar{P}\infty : \bar{P}\infty$ (macr.) $= 76° 16'$; $P : P$ (brach.) $= 136° 13'$; $P : P$ (macr.) $= 86° 15·2'$; $P : P$ (basal) $= 110° 5'$. No distinct cleavage. The index of refraction, for the brightest part of the spectrum, in the plane of the basal principal section, and for the ray polarised in this plane, is about 1·817. (W. H. Miller.)

OXALATES, $C^2Tl^2O^4$ and C^2HTlO^4.—Already described under OXALIC ACID (iv. 265).—*Cuprico-thallious oxalate*, $C^4Cu''Tl^2O^8.2H^2O$, crystallises from a solution of cupric carbonate in acid thallious oxalate, or from a mixed solution of cupric oxalate and neutral thallious oxalate, in slender flattened needles; it is partly decomposed by recrystallisation. (Willm.)

PHENATE, C^6H^5TlO.—Precipitated as a crystalline powder, on mixing a thallious salt with phenic acid. It is sparingly soluble in cold water, and crystallises from hot water in beautiful slender needles; melts without decomposition (F. Kuhlmann, Jun., Bull. Soc. Chim. [1864], i. 330).—The *phenylsulphamate*, or *sulphanilate*, is deliquescent, slightly soluble in alcohol, insoluble in ether, and crystallises very easily from a mixture of water, alcohol, and ether.

PHOSPHATES (Lamy, Ann. Ch. Phys. [4], v. 410).—The phosphates of thallium form a series nearly as complete as those of the alkali-metals, which they also resemble in their behaviour when heated. They are all colourless, nearly all easily soluble in water, and insoluble in alcohol. Their concentrated aqueous solutions yield, with nitric acid, a precipitate of thallious nitrate, and with caustic alkalis (but not with alkaline carbonates, or even with caustic alkalis in presence of carbonates), a precipitate of sparingly soluble trithallious orthophosphate.

Metaphosphate, $TlPO^3$.—This salt exists in two different modifications. The first remains on igniting monothallious orthophosphate, (TlH^2PO^4), as a vitreous opaline mass, very slightly soluble in water; its solution does not precipitate albumin directly, but only after addition of orthophosphoric acid. The second modification is obtained by igniting ammonio-thallious orthophosphate, as an easily soluble glass, whose solution is strongly acid, yields no crystals, but precipitates albumin immediately. It is also produced by fusing the insoluble modification with a few drops of orthophosphoric acid.

Orthophosphates.—The *monothallious salt*, TlH^2PO^4, is formed on mixing the dithallious salt with a quantity of phosphoric acid sufficient to give it an acid reaction. It crystallises from a solution concentrated by evaporation, in nacreous laminæ, easily soluble in water, insoluble in alcohol. It melts without alteration at 190°, and is converted, at a stronger heat, first into acid pyrophosphate, then, at a red heat, into metaphosphate.

The *dithallious salt*, Tl^2HPO^5, is produced by neutralising dilute phosphoric acid, at the boiling heat, with carbonate of thallium. The solution evaporated to a syrup first deposits crystals of the anhydrous salt, then other crystals containing $2TlHPO^4.H^2O$.—α. This hydrate, on account of its easy solubility, is difficult to obtain in well-defined crystals. It melts at 145°, without loss of weight, gives off its crystallisation-water with tumefaction at 170° (becoming also less soluble), and is converted, at a dull red heat, into vitreous pyrophosphate.—β. The anhydrous salt, Tl^2HPO^4, is easily soluble in the warm concentrated mother-liquor, but very sparingly in pure water, apparently suffering partial decomposition at the same time into monothallious and trithallious orthophosphate.

The *trithallious* or *normal salt*, Tl^3PO^4, first obtained by Crookes, is formed as a crystalline precipitate having a silky lustre, on mixing the saturated solutions of ordinary disodic phosphate and thallious sulphate (probably together with double phosphates of sodium and thallium, inasmuch as the liquid, after precipitation, exhibits an alkaline reaction); also, together with ammonio-thallious phosphate, on treating the mono- or di-thallious salt with excess of ammonia. By fusing 1 at. thallious metaphosphate with 2 at. thallious carbonate, as long as gas continues to escape, and pouring out the mass before it is quite solidified, trithallious orthophosphate is obtained, in needle-shaped crystals, one or two centimetres long. It melts, at a red heat, to a yellowish-red liquid, which solidifies at 10° to a white crystalline mass, of specific gravity 6·89. It is but sparingly dissolved by water, even at the boiling heat. According to Crookes, 100 pts. water dissolve 0·497 pt. of it at 15·5°, and 0·6712 pt. at 100°.

Ammonio-thallious orthophosphate crystallises from the mother-liquor of the trithallious salt in large transparent prisms. When ignited it leaves thallious metaphosphate.

Pyrophosphates.—The *dithallious* or *acid salt*, $Tl^2H^2P^2O^7$, produced by carefully heating monothallious orthophosphate, is extremely soluble in water, and crystallises from the acid solution in short prisms.—The *tetrathallious* or *neutral salt*, $Tl^4P^2O^7$, remains, on strongly heating hydrated dithallious orthophosphate (α), as a vitreous mass very soluble in water, and crystallises from the solution evaporated to a syrup, in confused needles, which are decomposed by water, with separation of a white precipitate. The anhydrous dithallious orthophosphate (β) yields the pyrophosphate with different properties—namely, as an opaque crystalline mass, whose solution yields, by evaporation, large prisms which are likewise decomposed by pure water. (Lamy.)

Picrate, $C^6H^2Tl(NO^2)^3O$.—Soluble in water, nearly insoluble in alcohol; crystallises, like the potassium-salt, in yellow needles, which have a silky lustre, and detonate strongly when heated.—The *picramate*, $C^6HTl(NH^2)(NO^2)^2O$, is a black-red crystalline precipitate, nearly insoluble in alcohol, and separating from boiling water in small regular crystals. (F. Kuhlmann, Jun.)

Racemate or **Paratartrate**, $C^4H^4Tl^2O^6$.—Very soluble in water; forms groups of crystals apparently belonging to the dimetric system. (Kuhlmann.)

Selenates and **Selenites**.—See pp. 229, 231.

Sulphates.—See p. 614.

Tartrates.—See p. 680.

Tungstate.—White powder, sparingly soluble in water; obtained like the molybdate. (Oettinger.)

Urate.—Obtained by double decomposition; almost insoluble in water. (Kuhlmann.)

Valerate, C^5H^9TlO.—Very soluble in water and in alcohol; resembles the acetate. (Kuhlmann.)

β. *Thallic Salts.*

Acetate, $Tl^2O^3.C^4H^6O^3.3H^2O$, or $Tl'''(C^2H^3O^2)^3.2Tl'''H^3O^3.\frac{3}{2}H^2O$.—Crystallises by spontaneous evaporation of a solution of thallic oxide in strong acetic acid prepared at the boiling heat, in colourless plates belonging to the rhombic system (sometimes accompanied by small prismatic crystals, probably of thallious acetate). These crystals, when exposed to the air, quickly turn brown on the surface; and are decomposed more quickly, at a gentle heat, into acetic acid and thallic oxide, the decomposition being nearly complete at 100°. The salt is also immediately resolved into its constituents by water. (Willm.)

Arsenate, $Tl'''AsO^4.2H^2O$.—Obtained, like the phosphate, as a lemon-yellow gelatinous precipitate, soluble in hydrochloric acid. Ammonia added to the solution throws down, first a bulky crystalline salt, which appears to differ from the preceding by its amount of crystallisation-water; on further addition, a yellow dithallic salt, and finally a brown precipitate. (Willm.)

Nitrate, $Tl'''(NO^3)^3$, separates from a concentrated solution, in colourless well-defined crystals containing 3 at. water (Strecker), 4 at. (Willm). The salt decomposes at 100°, with separation of brown thallic oxide.

Oxalate, $C^6\overset{\prime\prime\prime}{Tl}{}^2O^{12}$.—Obtained (mixed with thallious salt) as a white crystalline powder, nearly insoluble in water, by heating thallic oxide with aqueous oxalic acid or by precipitating a solution of a thallic salt with oxalic acid. (Willm.)

Ammonio-thallic oxalate, $C^4Tl'''(NH^4)O^8.3H^2O$, is formed, on mixing thallic sulphate with ammonium-oxalate, as a white precipitate, quite insoluble in cold water, and converted, by boiling with water, into thallious salt, with evolution of carbonic anhydride; when ignited it leaves fused metal. (Strecker.)

Phosphate, $Tl'''PO^4.2H^2O$. Separates, on diluting the solution of the nitrate mixed with phosphoric acid, "as a gelatinous precipitate, having a crystalline aspect." It is insoluble in water, but dissolves in strong nitric and dilute hydrochloric acid. Ammonia added to the latter solution throws down a green basic salt, $Tl^2O^3.2Tl'''PO^4.5H^2O$; afterwards brown thallic oxide.

Sulphate, already described (p. 614).

THALLIUM, PHOSPHIDE OF. Phosphoretted hydrogen passed through an ammoniacal solution of thallious sulphate, precipitates phosphide of thallium, as a black insoluble powder permanent in the air at ordinary temperatures.

THALLIUM, SELENIDE OF. Tl^2Se.—Obtained as a greyish-black mass, by fusing the two elements together in equivalent proportions (Lamy). By passing selenhydric acid gas into a solution of thallious carbonate, the same compound is precipitated in grey shining laminæ, which turn black on drying. It melts at 340°, and gives off selenhydric acid when treated with sulphuric or hydrochloric acid. (Kuhlmann, Jahresb. 1864, p. 253.)

THALLIUM, SULPHIDE OF. Tl^2S.—This compound is precipitated from all thallious salts by sulphide of ammonium, and from the acetate, carbonate, or oxalate by sulphydric acid (incompletely also from the nitrate, sulphate, or chloride), in dense flocks of a greyish or brownish-black colour. The precipitate oxidises in the air, and must therefore be washed with water containing sulphydric acid. It dissolves easily in dilute sulphuric or nitric acid, but is insoluble in sulphide of ammonium and cyanide of potassium. A cold (not too dilute) solution of thallious sulphate acidulated with a trace of sulphuric acid, yields, with sulphydric acid, shining black-blue laminæ of pure thallium-sulphide, appearing under the microscope to be made up of tetrahedrons, and more permanent than the amorphous sulphide (Hebberling). Thallic salts appear to be reduced to thallious sulphide by boiling with sulphide of ammonium. Sulphate of thallium projected into fused cyanide of potassium, is reduced to sulphide, which then forms a brittle metallic-looking mass, having the lustre of plumbago, and fusing more readily than metallic thallium.

THALLIUM-BENZAMIDE. C^7H^6TlNO.—Benzamide dissolves freely in a hot aqueous solution of thallious oxide, the excess crystallising out on cooling; and on adding a large excess of absolute alcohol to the filtrate, thallium-benzamide separates in fine needles, soluble, with alkaline reaction, both in hot and in cold water. It melts without decomposition. When moderately heated, it becomes dark at a higher temperature, and evolves white inflammable vapours, burning with a smoky greenish flame, and decomposes completely at a red heat, leaving fused oxide of thallium. Hydrochloric acid added to the aqueous solution, throws down protochloride of thallium, together with benzamide. (Church and Crookes, Chem. Soc. J. xvii. 151.)

THALLIUM-ETHERS. *Thallium-alcohols.* (Lamy, Compt. rend. lv. 286; Ann. Ch. Phys. [4], iii. 373; Jahresb. 1864, p. 463.)—Compounds formed by the action of thallium upon alcohols, analogous to those produced in like manner by the alkali-metals.

Thallium-amylate, $C^5H^{11}TlO$, is produced, though slowly, by the action of thallium on amylic alcohol; more readily by heating equivalent quantities of thallium-ethylate and amylic alcohol to 140°—150°, whereupon ethylic alcohol passes over first, then the excess of amylic alcohol, leaving the thallium-amylate in the form of a heavy oil, smelling like amylic alcohol, and having a specific gravity of 2·465 to 2·518. Its index of refraction for the line B is 1·572 at 20°. It does not solidify at 20°; dissolves easily in *amylic*, less easily in *ethylic alcohol*; with *chloroform* and *ether*, it behaves like the ethyl-compound (*infra*). When heated, it first gives off hydrogen, then amylic alcohol, and leaves a mixture of metallic thallium with thallious carbonate and valerate. It also decomposes, but less quickly, in contact with air or water. It burns with a white, moderately luminous flame.

Thallium-ethylate, C^2H^5TlO.—Produced, with evolution of hydrogen, when thallium and ethylic alcohol are heated together to 100° in a sealed tube (Church). Lamy prepares it by suspending thin plates of thallium within an exhausted bell-jar, over a shallow dish containing absolute alcohol, and passing pure oxygen-gas (free from water and carbonic anhydride) into the jar. At 20°—25°, the thallium is converted, within 24 hours, with simultaneous formation of water, into ethylate of thallium, which collects in the dish. After being freed from excess of alcohol, by heating to 100°, it remains as an oil of specific gravity 3·480—3·553, being, next to mercury, the heaviest liquid known. Its expansion-coefficient, between 0° and 100°, is 0·072. At $-3°$ it solidifies, with considerable contraction of volume. By prolonged heating, or by keeping in a vacuum, it suffers partial decomposition, becoming brown, increasing in density to 3·685, and requiring a greater degree of cold to solidify it. In refractive and dispersive power, it exceeds all other liquids, as shown by the following numbers (determined for a temperature of 20°):—

		Refractive power.			Dispersive power.
		Line B.	Line D.	Line H.	
Thallium-ethylate, specific gravity	3·550	1·6615	1·6676	1·7159	0·0975
" " " "	3·612	1·6725	1·7170	1·7678	0·0958
Carbonic disulphide . .	. .	1·6140	1·6330	1·6935	0·0795

Thallium-ethylate dissolves in about 5 pts. of absolute *alcohol*; if the alcohol is not quite anhydrous, white thallious hydrate is deposited. With pure *ether* free from air, it forms a clear solution; with ether containing water, the liquid soon becomes yellowish or brown, and deposits radio-crystalline thallious hydrate, which gradually turns brown. This reaction is so delicate, that it may be used as a test for the purity of ether. Thallium-ethylate likewise dissolves freely in *chloroform*; but the solution soon becomes turbid, and deposits crystallised protochloride of thallium, together with a substance which colours the latter dark-red, and is very sensitive to light; the liquid, which has become strongly acid, contains a salt of formic acid.

Thallium-ethylate, when heated, gives off hydrogen slightly at 130°, regularly between 170° and 180°, alcohol distilling over at the same time, thallium being deposited in shining laminæ, and a strongly alkaline residue being left containing thallious carbonate and acetate. Above 200°, carbonic oxide and carbonic dioxide are given off, together with small quantities of acetone and acetic acid. Thallium-ethylate decomposes when exposed to the *air*, and still more quickly in contact with *water*, yielding alcohol and thallious hydrate. On keeping it (best under a layer of absolute alcohol), the sides of the vessel become gradually coated with black thallious oxide. When set on fire by the flame of a candle, it burns with a green, slightly luminous flame, leaving black thallic oxide and metallic thallium.—*Potassium* and *sodium* slowly separate metallic thallium from it, but it is not decomposed by iron, zinc, lead, or even by the electric current.—With *sulphuric* or *hydrochloric acid*, it yields alcohol and a thallious salt; dry *carbonic dioxide* unites directly with it, forming a white solid body, which is resolved by heat into metallic thallium and empyreumatic products. When thallium-ethylate is suddenly mixed with *carbonic disulphide*, a violent action takes place, resulting in the formation of a black sulphur-compound; but if the thallium-ethylate be slowly dropt into the carbonic disulphide, a bulky, yellowish, gelatinous mass is formed. (Lamy.)

Thallium-methylate, CH^3TlO, is formed, in small quantity only, by the process which yields the ethyl-compound, but it is very easily obtained by treating ethylate or amylate of thallium with excess of methylic alcohol. Considerable rise of temperature then takes place, and methylate of thallium separates as a white solid substance, which, by fusion and cooling under the liquid, may be crystallised in thick oblique prisms. When quickly pressed between filter-paper, and dried in a vacuum in contact with a few lumps of sodium, it forms a white solid mass, alterable in contact with the air, about five times as heavy as water, slightly soluble in *methylic alcohol* and in *ether*, somewhat more soluble in *chloroform*. When heated, it gives off a large quantity of carbonic oxide, together with hydrogen and methylic alcohol; and when set on fire, it burns with a flame strongly tinged with green.

On *thallium-phenylate*, see p. 755; on the compounds of *thallious chloride* and *bromide* with *ethers*, pp. 747, 748.

THALLIUM-GLASS. By substituting thallium for lead, or for potassium, in the preparation of flint-glass, glasses are obtained of great density and refracting power. By fusing together 300 pts. of sand, 200 of minium, and 333 carbonate of thallium, a perfectly homogeneous glass was obtained, having an agreeable yellow tint, and very brilliant. Its density was 4·233, and its index of refraction (for the yellow ray) 1·71; it is therefore denser and more refractive than any glass hitherto known. By altering the proportions of thallium, glasses have been obtained, varying in density from 4·235 to 5·025, and having indices of refraction ranging from 1·71 to 1·965. (Lamy, Bull. Soc. Chim. [1866], i. 164.)

THALLIUM-TRIAMINE. $N^3Tl'''H^6$.—Thallic oxide dissolves in sal-ammoniac at the boiling heat, and the cold concentrated solution yields with ammonia a heavy white precipitate, consisting of $TlCl^3.3NH^3$, or probably *hydrochlorate of thallium-triamine*, $N^3Tl'''H^6.3HCl$. It is decomposed by water, yielding thallic oxide and sal-ammoniac:

$$2(TlCl^3.3NH^3) + 3H^2O = Tl^2O^3 + 6NH^4Cl.$$

When heated in a sealed tube, it is resolved into ammonia, an ammonium-salt, and a chloride of thallium, probably Tl^2Cl^3. Its solution in hydrochloric acid yields cubic or octahedral crystals of the double salt, $3NH^4Cl.TlCl^3$. (Willm, Jahresb. 1863, p. 251; 1864, p. 251.)

THALLOCHLORE. A name applied by Knop and Schnedermann (Ann. Ch. Pharm. lvi. 147, 154) to the green colouring-matter of lichens, which they regard as different from ordinary chlorophyll.

THARANDITE. Syn. with BITTER SPAR (i. 600).

THEBAINE. $C^{19}H^{21}NO^3$. *Paramorphine.* (Pelletier, J. Pharm. xxi. 569.—Couerbe, Ann. Ch. Phys. [2], lix. 155.—Kane, Ann. Ch. Pharm. xix. 9.—Anderson, *ibid.* lxxxvi. 179.)—An organic base existing in opium. It was discovered in 1835 by Pelletier, who obtained it by treating the extract of opium with milk of lime in excess, washing the calcareous precipitate with water, and exhausting it, after drying, with boiling alcohol. The alcoholic solution leaves on evaporation a residue, from which thebaine may be dissolved out by ether.

Anderson obtains thebaine from the mother-liquors of the preparation of narcotine. The alcoholic liquor from which the first strongly-coloured crystals of narcotine have been deposited, yields by evaporation, an amorphous residue consisting of a large quantity of resin, a little narcotine, and all the thebaine contained in the opium. This residue is treated with boiling dilute acetic acid, which dissolves the alkaloïds, together with a small quantity of resin; and on adding basic acetate of lead to this solution, in sufficient quantity to render it distinctly alkaline, all the narcotine and resin are precipitated, while the thebaine remains in solution. The liquid is filtered; the excess of lead removed by sulphuric acid; the thebaine contained in the filtered liquid is precipitated by ammonia; this precipitate, after being washed, is dissolved in boiling alcohol, and the solution is treated with animal charcoal. It then, on cooling, deposits thebaine in shining scales, which may be purified by recrystallisation.

Thebaine crystallises from solution in alcohol or ether, in square scales having a silvery lustre. Its taste is acrid and styptic rather than bitter. It is extremely poisonous; Magendie found that 5 centigrammes of it injected into the jugular vein of a dog produced tetanic convulsions, quickly followed by death. Thebaine is insoluble in water, very soluble in alcohol and ether, especially when warm, insoluble in aqueous potash and ammonia; it dissolves rapidly in acids. It contains, according to the mean of closely-agreeing analyses by Kane and Anderson, 73·10 per cent. carbon, 6·96 hydrogen, and, according to Anderson, 4·43 per cent. nitrogen. The formula $C^{19}H^{21}NO^3$, requires 73·31 per cent. carbon, 6·75 hydrogen, 4·50 nitrogen, and 15·44 oxygen.

Thebaine melts at 12·5°, and decomposes at higher temperatures. It is coloured deep red by strong *sulphuric acid*. According to Dragendorff (Jahresb. 1864, p. 728), sulphuric acid, whether pure or containing nitric acid, colours it deep red to orange, gradually changing to olive-green at 150°. Sulphuric acid of specific gravity 1·3 dissolves it in the cold; but the solution, when gently heated, deposits a resinous substance, which dissolves slowly on boiling with water, and is deposited on cooling in microscopic, slightly soluble crystals, apparently a product of decomposition (Anderson).—Concentrated *nitric acid* acts strongly on thebaine, even in the cold, giving off red vapours, and forming a solution, which, when mixed with potash, becomes dark-coloured and gives off a volatile alkali.—Thebaine also dissolves easily in *hydrochloric acid*; the solution becomes dark-coloured when evaporated, and leaves a resinous residue no longer quite soluble in water.—*Chlorine* and *bromine* act strongly on thebaine, forming resinous products.

Thebaine-salts do not crystallise from aqueous solution.

The *hydrochlorate*, $C^{19}H^{21}NO^3.HCl.H^2O$, is obtained by mixing thebaine with a small quantity of strong alcohol, and adding alcoholic hydrochloric acid till complete solution is effected, avoiding an excess of acid; it then separates on standing in rhombic crystals. It is very soluble in water, the solution resinising on evaporation; slightly soluble in alcohol, and insoluble in ether.—The *chloroaurate* is an orange-red precipitate, which melts to a resinous mass at 100°.—The *chloromercurate* is a white crystalline precipitate, obtained with hydrochlorate of thebaine and mercuric chloride; with free thebaine a bulky precipitate is obtained, which, as well as the crystalline precipitate, is of variable composition.—The *chloroplatinate*, $2(C^{19}H^{21}NO^3.HCl).PtCl^4.2H^2O$, is precipitated on adding platinic chloride to hydrochlorate of thebaine. It is slightly soluble in boiling water, the solution depositing a salt, which appears to be a product of decomposition.

The *sulphate* is obtained by adding sulphuric acid to an ethereal solution of thebaine, partly in the crystalline state, partly as a resin, which becomes crystalline on standing.

THEBOLACTIC ACID. This name is applied, by T. and H. Smith, to an acid, isomeric or identical with lactic acid, discovered by them in the mother-liquors of morphine. To prepare it, the mother-liquor of morphia, after having been freed from all organic bases by precipitation with an alkali, is digested with oxide of lead; the evaporated liquid is mixed with a large quantity of alcohol and sulphuric acid; and the solution filtered from the precipitated sulphates, and saturated with milk of lime, is evaporated to a syrup; this, after some time, solidifies to a crystalline mass of calcic thebolactate. Turkey opium yields about 2 per cent. of this salt.

Thebolactic acid appears, from an analysis of the silver-salt by Dr. Stenhouse, to have exactly the same percentage composition as lactic acid; but (according to T. and H. Smith) its copper- and morphine-salts differ in crystalline character from the corresponding lactates, and the behaviour of ferric thebolactate with ammonia is different from that of ferric lactate. (Pharm. J. Trans. [2], vii. 50; also private communication from Messrs. T. and H. Smith.)

THEINE. Syn. with CAFFEINE (i. 707).—According to Attfield (Pharm. J. Trans. [2] vi. 457), the nuts of the kola-tree (*Cola acuminata*), which in the fresh state are used in the western part of Central Africa as food and medicine, contain theine, the dried nuts yielding about 2 per cent.

THEIOTHERMIN. Syn. with BAREGIN (i. 500).

THENARDITE. Native anhydrous sulphate of sodium. (See SULPHATES p. 610.)

THENARD'S BLUE. A blue colour prepared by igniting a mixture of cobalt phosphate or arsenate and alumina. (See PHOSPHATES, iv. 500.)

THEOBROMA. See CACAO (i. 700).—The ash of several parts of the cacao-tree, from the plantations of Manado, in Celebes, has been examined by Rost van Tonningen (Rép. Chim. app. ii. 261), with the following results:

	Bark.	Leaves.	Fruit.	Seed.
Ash per cent. of the dried substance (? at 100°)	12·86	14·58	13·34	3·87
Composition of the ash:				
Silica	34·60	42·65	trace	0·99
Sulphuric anhydride	4·85	10·22	3·50	4·30
Chlorine	0·63	0·25	0·30	0·45
Phosphoric anhydride	23·01	5·21	7·14	38·18
Lime	11·65	14·38	3·76	1·94
Magnesia	4·56	6·19	3·21	trace
Carbonate of calcium	19·53	20·13	69·70	44·44
Carbonate of sodium	trace	trace	8·66	7·83
	98·83	99·03	96·27	98·13

THEOBROMINE. $C^7H^8N^4O^2$. (Woskresensky, Ann. Ch. Pharm. [1841], xli. 125.—Glasson, *ibid.* lxi. 335.—Keller, *ibid.* xcii. 71.—Rochleder, *ibid.* xxi. 9; lxxxix. 124.—Strecker, *ibid.* cxviii. 151.)—An organic base existing in cacao-beans. To prepare it, the beans are treated with water for some time at the heat of the water-bath; the solution is strained through linen, and carefully precipitated by neutral acetate of lead; the precipitate, which is abundant, is separated by filtration; and the filtered liquid is freed from excess of lead by sulphuretted hydrogen. The filtrate then yields by evaporation a brown residue, which is boiled with alcohol, and filtered at the boiling heat; the liquid, on cooling, deposits a reddish-white crystalline powder, which is obtained colourless by repeated crystallisation (Woskresensky; Glasson). Keller heats the theobromine, obtained as above, between two watch-glasses, whereby a small quantity of charcoal is separated, and a dazzling white sublimate formed.

Properties.—Theobromine is a colourless crystalline powder, composed of microscopic trimetric crystals, exhibiting the combination $\infty \bar{P}2 . P$, and arranged in club-shaped groups (Keller). It tastes very bitter, but the flavour is very slowly developed. Sublimes, without decomposition, between 290° and 295°. Its composition is shown by the following analyses:—

		Calculation.	Woskresensky.	Glasson.	Keller.
C^7 . . .	84	46·67	46·33	47·13	46·28
H^8 . . .	8	4·44	4·55	4·60	4·80
N^4 . . .	56	31·11	35·38	31·27	30·86
O^2 . . .	32	17·78	13·74	17·00	18·06
$C^7H^8N^4O^2$ . .	180	100·00	100·00	100·00	100·00

Theobromine is sparingly soluble in *hot water*, still less soluble in *alcohol* and in *ether*. The aqueous solution forms, with *mercuric chloride*, a white crystalline precipitate, slightly soluble in water and in alcohol. (Woskresensky.)

Decompositions.—1. Theobromine heated with *peroxide of lead* and dilute *sulphuric acid*, gives off carbonic anhydride, the decomposition, when once begun, going on without further application of heat; and if the right quantity of peroxide of lead be added, and the heating not too long-continued, there is obtained, after separating the sulphate of lead by filtration, a transparent colourless liquid, which gives off ammonia when treated with potash, separates sulphur from sulphuretted hydrogen, colours the skin purple-red, and immediately turns blue when treated with magnesia. An excess of magnesia destroys this colour, which may, however, be restored by cautious addition of sulphuric acid. The liquid, mixed with excess of magnesia, becomes reddish, and gives off ammonia during evaporation to dryness; boiling alcohol extracts from the residue a body which crystallises from the solution in rhombic prisms, is soluble in alcohol, has an acid reaction, and does not precipitate chloride of mercury, nitrate of silver, or tetrachloride of platinum. (Glasson.)

2. It dissolves in boiling *baryta-water* without evolution of ammonia; the solution, on cooling, solidifies to a white jelly.

3. With *chlorine*, in presence of water, it forms amalic acid and hydrochlorate of methylamine (Rochleder and Hlasiwetz, Wien. Akad. Ber. 1850, i. 266).—4. Heated with *potash*, it gives off methylamine.

5. The silver-compound of theobromine, heated to 100° with *iodide of methyl*, yields silver-iodide and caffeine:

$$C^7H^7AgN^4O^2 + CH^3I = AgI + C^8H^{10}N^4O^2.$$

Hence caffeine may be regarded as methylated theobromine. (Strecker.)

Argentic Theobromine, $C^7H^7AgN^4O^2$.—When theobromine is dissolved in ammonia (in which it dissolves much more easily than in water), and nitrate of silver is added, a gelatinous precipitate is obtained, which dissolves easily in warm ammonia. On boiling the solution for some time, ammonia escapes, and a colourless granular precipitate of argentic theobromine is formed, which is nearly insoluble in water. The precipitate contains water, which is given off slowly over oil of vitriol, or at 100°, more quickly at 120°—130°. The residue may be heated to 160° without alteration; at a higher temperature it does not melt, but decomposes, and gives off vapours, which condense to unaltered theobromine. (Strecker.)

Theobromine Salts.—Theobromine is a weak base, but nevertheless forms salts which crystallise well, though they are somewhat unstable, the neutral salts being decomposed by water, and converted into basic salts.

Hydrochlorate, $C^7H^8N^4O^2.HCl$.—Theobromine dissolves readily in concentrated hydrochloric acid; and as the warm solution cools, the salt separates in crystals, which may be dried over oil of vitriol and caustic potash. It gives off all its hydrochloric acid at 100°, and decomposes with water, forming a basic salt (Glasson).—The *chloroplatinate*, $2(C^7H^8N^4O^2.HCl).PtCl^4.4H^2O$, separates from a mixture of the hydrochlorate and platinic chloride, in monoclinic prisms, exhibiting the faces ∞P and oP. It is efflorescent, gives off its water of crystallisation at 100°, decomposes at a stronger heat, and, when ignited in the air, leaves pure platinum.

The *nitrate*, $C^7H^8N^4O^2.HNO^3$, separates from a solution of theobromine in warm nitric acid, on cooling, in monoclinic prisms, which give off their acid at 100°, and are easily decomposed by water.

The *argentic nitrate*, $C^7H^8N^4O^2.AgNO^3$, separates from a very dilute solution of nitrate of theobromine mixed with nitrate of silver, in shining silver-white needles, very sparingly soluble in water. It does not undergo any perceptible loss at 100°, but at a higher temperature, it melts and gives off nitrous acid, and on ignition leaves metallic silver.

THERMOBAROMETER. This name was applied by Bellani to a syphon-barometer having its two wide legs united by a narrow tube, so that it could be used either in its ordinary position as a barometer, or in the reversed position as a thermometer, the wide sealed leg of the barometer then serving as the bulb of the thermometer.

The same name is sometimes applied to a thermometer which indicates the atmospheric pressure by the boiling-point of water.

THERMO-ELECTRICITY. See ELECTRICITY (ii. 412).

THERMOMETER (θερμός, hot; μέτρον, measure).—The thermometer measures the *temperature*, or *degree of hotness*, of a body; it thus determines one dimension, so to speak, of the quantity of heat within the body—the specific heat and the weight of the body being the other dimensions. The measurement is founded on the law, that perfect gases tend to expand with equal increments of volume for equal increments of heat. Mercury, being compared with gases, is found to follow nearly the same law at ordinary temperatures. It is likewise almost perfectly adapted for thermometric purposes, from its wide range of liquidity (390° C.), its low specific heat, its high conducting power, and its uniform purity.

As the thermometer is the most important and indispensable of all instruments in most physical researches, too much attention cannot be paid to attaining perfection in its manufacture and use.

Thermometer Tube.—In making a mercurial thermometer, a capillary glass-tube, usually of flat or elliptical bore, is first to be selected, as free as possible from all visible defects. It must be of almost perfectly uniform bore throughout. That it is so is to be ascertained by introducing enough mercury to fill about one inch of the tube, and observing if the length of this mercurial column remains almost unchanged as the mercury is forced through the tube. If the tube be not perfectly clean internally, nitric acid or other solvents may be introduced, the interior of the tube being afterwards thoroughly washed with distilled water, and dried by drawing air through it when hot.

A bulb is now to be formed by sealing and softening the tube at one end, in the blowpipe-flame, and then forcing dry air in by means of a small elastic bottle fixed to the open end, and compressed by the fingers. Much skill, of course, is required in this operation, and the ultimate character of the instrument will vary with every particular manner of heating the glass.

The form of the bulb, too, is a matter for much consideration. Its capacity must have such a ratio to the capacity of the tube, that the degrees may be long enough to read with the required precision, and not much longer. Thus, thermometers intended to show the $\frac{1}{10}$ of a degree (Fahr.), should have degrees not less than $\frac{1}{10}$ inch in length.

Fig. 799.

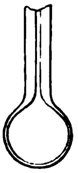


Fig. 800.

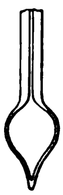


Fig. 801.

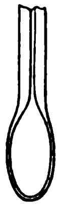


Fig. 802.

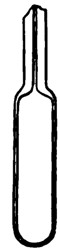
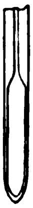


Fig. 803.



The required capacity of the bulb may be calculated as afterwards shown. The ordinary shape of the bulb is spherical (*fig.* 799), and this is the best suited to bear the pressure of the atmosphere without shrinking. But an elongated bulb, either pear-shaped (*figs.* 800 and 801), or tubular (*figs.* 802 and 803), exposes a much larger surface for the conduction of heat, in proportion to its capacity, and is therefore favourable to sensitiveness. A bulb, too, of no greater diameter than the tube, is less liable to be broken, and, for chemical purposes especially, is convenient and neat. The thickness of the glass is an important point; if too thin, it may yield to the atmospheric pressure, so as to raise the zero of the instrument; if too thick, the instrument will be insensitive. In all these points a thermometer should be specially adapted to its intended employment.

Fig. 804.

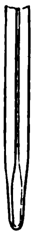


Fig. 805.

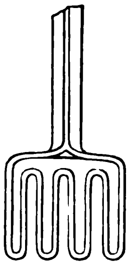
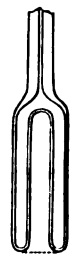


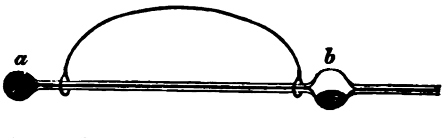
Fig. 806.



Extremely sensitive and yet exact thermometers have lately been prepared by the best London makers. In these, either the bore of the tube is very minute, and the bulb consequently small (as in *fig.* 804), or the bulb is made to contain much mercury, and shaped into a long cylindrical tube, bent into some convenient form, as in the *Gridiron* thermometer of Negretti and Zambra (*fig.* 805). In *fig.* 806 is shown a suggestion of Mr. Beckley, of the Kew Observatory, for increasing the surface of thermometer-bulbs without impairing their inflexibility. The mercury is contained between two concentric glass-cylinders, of which the inner one is open at the bottom.

Filling the Tube.—The following is the most perfect mode of filling the thermometer with mercury:—A sufficient length of the tube, *a b*, is marked off to form the stem of the thermometer, and a second bulb, rather larger than the first, is roughly blown at *b*. When the bulb is half-cooled, the open end of the tube is held in pure and well-boiled mercury, which gradually rises into the first bulb. By inverting the position of the tube, and alternately heating and cooling the lower bulb (*a*), sufficient mercury may be made to pass from *b* into *a*, almost to fill *a*, a little remaining over in *b*. The whole tube is now held by the wire-handle shown in *fig.* 807, over a charcoal-fire or a series of powerful gas-burners, so as to be strongly and uniformly heated throughout its whole length. The mercury boils easily, and its vapour drives out every trace of air or moisture. When this is thoroughly accomplished, and the mercury yet boiling, the open end of the tube, which must not be very hot, is thrust against a piece of sealing-wax, and then at once withdrawn from the heat. As the tube cools, a little wax is drawn in, and, in time becoming solid, prevents the entrance of any air. When quite cool, the mercury perfectly fills the whole of the lower bulb and tube. Let the tube be now inclined, and the lower bulb raised to a temperature rather higher than the thermometer is intended ever to indicate. A part of the mercury is thus expelled, and as the column

Fig. 807.



begins to retreat again on cooling, the tube is to be melted and hermetically sealed, just below the bulb *b*, which is drawn off. The perfection of the vacuum thus produced within part of the tube, may be known by the mercury running freely up and down, especially if the tube be not very fine. This process is more simply but less perfectly performed by some makers, who omit the second bulb, and place the mercury in a little funnel of glass or paper affixed to the open end of the tube.

Graduation.—A common thermometer is usually graduated by determining two points of the scale, by comparison with a standard thermometer, and dividing the interval into the proper number of equal parts. The thermometric scales usually employed are well known to be three in number, and are thus defined:—

	Temperature of melting ice.	Interval.	Temperature of boiling water.
Centigrade scale (C.)	0·0°	100·0°	100·0°
Fahrenheit's scale (F.)	32·0°	180·0°	212·0°
Reaumur's scale (R.)	0·0°	80·0°	80·0°

Of these, the Centigrade is in general use on the Continent, and is so far superior to our own Fahrenheit's scale, that all scientific chemists should at once adopt it. It is already adopted in many English scientific treatises. Reductions from one scale to the other are easily made by the following formulæ:—

Fahrenheit to Centigrade	$\frac{5}{9}(F.^\circ - 32) = C.^\circ$
Centigrade to Fahrenheit	$\frac{9}{5}C.^\circ + 32^\circ = F.^\circ$
Reaumur to Fahrenheit	$\frac{9}{4}R.^\circ + 32^\circ = F.^\circ$

The Reaumur scale being seldom met with, the numbers 5, 9, and 32, which are sufficient for the reduction of Fahrenheit and Centigrade, may be easily remembered and applied.

Mounting of the Thermometer.—For chemical purposes, the simple tube-thermometer, with the divisions etched upon it, is by far the best. For accurate purposes, indeed, divisions upon the glass are alone to be trusted; and if an ivory scale is attached at all, it must only be used to show the whole degrees with quickness and security from mistake.

For meteorological use, the degrees should still be etched on the glass, but may be repeated on the metal scale. In this respect the Kew Observatory common thermometer leaves nothing to be desired. It may be had from the best opticians, with a certificate of its comparison at Kew, at the price of about half-a-guinea. More sensitive instruments are mentioned in describing the Dry and Wet Bulb Hygrometer. (See HYGROMETER, iii. 228.)

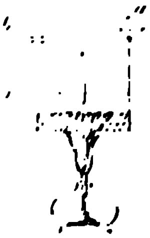
Standard Thermometer.—We shall describe the graduation of a standard thermometer as it was practised by Mr. Welsh at the Kew Observatory of the British Association, on the principles proposed by Regnault, and described at considerable length by Pierre (Ann. Ch. Phys. [3], v. 428).—Welsh. (*Report to Royal Society* Phil. Mag. [4], iv. 306.)

Calibration of the Tube.—A tube, having been selected as tolerably free from all visible defects, a short column of mercury, generally less than one inch long, is introduced. The tube is then attached to a dividing-engine, and either end put in communication with an elastic bag compressed by a screw, by which means the mercury can be moved at will. Commencing at one end of the desired scale, the mercury is made to coincide with cross-wires in the focus of a microscope carried by the cutting slide of the engine. By turning the screw until the wires correspond with the other end of the column, we learn the length of the column in revolutions of the screw. The mercury is now moved until its other end exactly coincides with the cross-wires which have remained stationary. The length of the column is again measured, the difference, if any, indicating inequality of the tube. The same process is repeated, until the column has been measured for each length of itself through the whole extent of the proposed scale. Permanent marks are made on the glass, at the points of commencement and ending of the calibration.

Graduation.—The measured lengths of the column of mercury, in its successive steps along the tube, corresponding to equal volumes, we may assume, unless the tube is a very faulty one, that the calibre of the tube is uniform throughout each length. Hence we may divide the length of each, as expressed in revolutions of the screw, into any convenient number of parts, and proceed to the graduation, starting from one end, and successively adding on the requisite number of revolutions. The divisions are cut with a fine needle-point upon a coating of engravers' wax, and afterwards etched with hydrofluoric acid. By weighing a measured column of mercury, we have data to calculate the capacity of the bulb most suitable for our intended thermometer.

[illegible] placed in [illegible]

[illegible] zero [illegible], Pierre [illegible] taken before the freezing-point, but we think that, for most purposes, the order should be reversed. It is best, however, to take the freezing- and boiling-points with as long an interval between as possible, the thermometer being left undisturbed at the ordinary temperature of the air before each determination.



As the boiling point of water depends entirely on the pressure of the air at the time, the barometer must be properly read. If it stand at 0·760 millimetre (or 30 English inches) when properly corrected (see BAROMETER, i. 512), the temperature of boiling water is exactly 100° C. (212° Fahr.). If not, the temperature must be calculated, allowing a change of ± 1° C. for every divergence of pressure equal to ± 26·7 millimetres (or 1·71° Fahr. for every inch of pressure). It is better, however, to use the following table, which gives the barometer reading (corrected) corresponding to every tenth of a degree near 100° Centigrade:—

Boiling-point °Cent.	Reading of Barometer. Millim.	Boiling-point °Cent.	Reading of Barometer. Millim.
98·8	727·96	99·5	746·50
98·9	730·58	99·6	749·18
99·0	733·21	99·7	751·87
99·1	735·85	99·8	754·57
99·2	738·50	99·9	757·28
99·3	741·16	100·0	760·00
99·4	743·83	100·1	762·73

To obtain a still nearer approximation, proportional parts of the differences may be taken. Thus, suppose a thermometer with an arbitrary scale to read 187·5 in the boiler with the barometer at 755·03; the corresponding temperature is $99{\cdot}8 + \frac{755{\cdot}03 - 754{\cdot}57}{757{\cdot}28 - 754{\cdot}57} \times {\cdot}1 = 99{\cdot}82$. Suppose the freezing-point on the arbitrary scale to be 25·4: then 187·5 − 25·4, or 162·1 arbitrary divisions, are equal to 99·82° Cent., or 162·4 divisions to 100°. Thus, 25·4 + 162·4, or 187·8, is the true degree 100, or the boiling-point for the pressure 760 millim.; and the value of any arbitrary degree n is $(n - 25{\cdot}4)\frac{100}{162{\cdot}4}$.

Examination of a Thermometer.—Any good thermometer, of which the scale extends from 32° to 212°, may be made to serve as a correct standard thermometer, by direct experiment, if it be worth while to take the necessary trouble. We will suppose the thermometer to be already graduated. By placing it in melting ice and above boiling water, with the precautions already described, we first ascertain the errors of the degree 32°, and of some point near 212°. At the intermediate points, the error is then found by the following process of Professor Forbes (Phil. Trans. cxxvi. [1836], p. 578), which is that of Bessel (Tilloch's Phil. Mag. [1824], lxiii. 307) simplified and improved:—

Detach a column of mercury from the rest, of such a length as to be nearly an aliquot part of 180°. In a tube of moderately wide bore, the length of the column may be adjusted, with great accuracy, by bringing it just into contact with the remainder of the mercury, and at the same time heating or cooling the bulb. A part of the mercury will then slowly pass over, one way or the other. This column is then caused to *step* along the tube, beginning at 32°, the one end being brought to the exact point which the other had previously occupied, this point being carefully noted in respect to the nearest graduation-mark. The capacity of the tube is thus measured out into exactly equal portions, just as a length is measured by a carpenter's rule. The column may be moved and adjusted to its position, with any degree of accuracy, by tapping one end or other of the tube or scale.

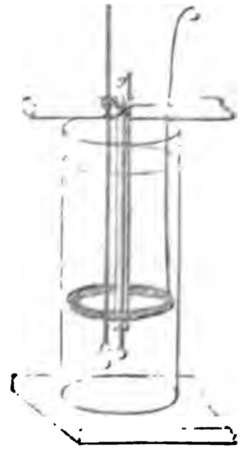
The end of the measuring column will finally fall near to 212°. Let it fall at $212 + c$, in which c is either + or −. Also let the number of intervals measured be n, and the corrections for 32° and 212°, already determined, be a and b (+ or −) Then, neglecting the very slight error which may exist in the portion of the tube by which the small quantity c was measured, the true interval corresponding to the length of the column will be $\frac{180^\circ - a + b + c}{n} = \mathrm{I}$, and the true temperatures corresponding to the divisions noted in the scale at the successive steps will be $32^\circ + a + \mathrm{I}$, $32^\circ + a + 2\mathrm{I}$, and so on up to $32^\circ + a + n\mathrm{I}$.

Several determinations may be made in this way with columns of different lengths. The results may then be projected into a curve.

This process of Professor Forbes may be performed in two or three hours, the freezing- and boiling-points having previously been determined, and the Professor considers it easier than comparison with a standard. It is scarcely applicable, however, to thermometers of very fine bore.

Comparison of Thermometers.—The mode in which thermometric accuracy will doubtless be most generally attained, is by comparing each thermometer used against a standard one, or even against a good thermometer, previously carefully compared with a standard. This comparison is very easily performed at all ordinary temperatures, as follows:—The standard thermometer and that which is to be compared, are firmly tied to a cross-piece of wood or other support, in such a manner that the bulbs shall hang in exactly the same level plane, and as near each other as is safe. They are then placed in the axis of a cylindrical glass vessel 12 or 15 inches deep, and 8 or 9 in diameter. Sufficient water is poured in to cover the whole of the mercurial columns, and it must be of the highest temperature at which it is desired to make the comparison. As water tends to arrange itself in layers of different temperature, agitation must be actively maintained, by moving up and down within the vessel, the ring-shaped agitator shown in *fig.* 809. This may be formed of stout wire, with a strip of calico roughly twisted round the ring part, which, being made nearly of the same diameter as the glass vessel, cannot touch the thermometer.

Fig. 809.



After brisk agitation, the readings of the thermometers are rapidly taken through the water, almost in the same moment, and at once recorded. In doing this, the observer should give his chief attention to the decimal parts of degrees, for the number of whole degrees can be taken afterwards at leisure, and any mistake in these will easily be apparent on taking the differences. The purpose of this haste is, of course, to avoid any error from the cooling of the water between the two readings. This error may be further eliminated by inverting the order of the readings each time. The water having been allowed to cool a few degrees, it must again be briskly agitated before the next pair of readings are taken, and so on with each successive step. Error might be still further eliminated, if necessary, by repeating the whole operation with a rising instead of a falling temperature, produced either by successive additions of hot water, or by a source of heat placed under the glass vessel.

It is, of course, possible to compare two or more thermometers with the standard at the same operation; but the chances of mistake and error from cooling increase in such a high degree with the number compared, that we strongly recommend the reader never to read more than two thermometers and the standard at the same time. In the Kew Observatory, indeed, where large numbers of thermometers are constantly compared for meteorological purposes, Mr. Welsh has devised a revolving vessel and stand, by which, with the aid of an assistant, he was able to read six thermometers at once. (Phil. Mag. [4], iv. 309.)

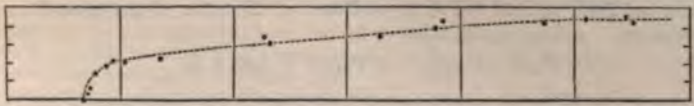
We think that the results of this process, performed rigorously as we have described it, are capable of almost any degree of accuracy, from the boiling point of water down to low temperatures, at which solutions or other liquids cooled by freezing mixtures may be used. **Professor Forbes**, however, objects to it (Brit. Assoc. Report, 1840, p. 49), and remarks that where the investigation is an important one, constant sources of heat, natural or artificial, cannot be too carefully sought. Bark-pits, natural hot springs, waste hot water of steam-engines, and the boiling-points of some liquids, such as alcohol, may be usefully employed.

When some determinations of especial importance and exactness, as of a melting- or boiling-point, have to be made at or about a particular temperature, the best mode is to compare the thermometers used with one or more standards, in media of the constant but required temperature, such as boiling alcohol diluted up to a certain point. **Herschel** (Admiralty Manual of Scientific Enquiry, p. 293) states that the best mode of ensuring perfect identity of temperature in comparisons is long rest of the thermometers in contact, in a box stuffed with cotton, the parts of the scales to be read off being occasionally uncovered for that purpose. This process would be a very slow one, but otherwise unexceptionable. It is almost needless to mention that comparisons of thermometers in the open air are useless for exact purposes.

Mr. Welsh gives a mode of examining the lower part of a thermometer *scale* without the use of freezing mixtures, but it is open to exception.

Change of the Zero-point.—A serious difficulty is thrown in the way of thermometric accuracy by the fact, that the zero of the instrument, by which may be meant any determinate point selected for verification, but generally the position of the mercury in melting ice (32° Fahr.), can seldom be considered invariable in the best instruments, and is more properly described by Despretz as in *continual oscillation*. These movements are of two kinds:—1. A gradual, continued, and permanent rise of the zero-point. This phenomenon has been studied by **Despretz** (Ann. Ch. Phys. [2], lxiv. 312), who, among other experiments, frequently determined the freezing-point of a thermometer during five years. We have shown the results graphically in *fig.* 810, and in spite of irregularities, due to the fact that the thermometer was in constant and various use during the period, the curve produced is sensibly a parabola. Professor W. H. Miller, in correcting the readings of a standard thermometer, found that the rise of the zero-point was represented with sufficient accuracy by a formula

Fig. 810.



($0{\cdot}0044 \times m^2$), which would give a hyperbolic curve. It is generally supposed that the rise of the zero-point is due to the atmospheric pressure, although Legrand (Ann. Ch. Phys., &c., [2], lxiii. 372) disputes this, and attributes it to molecular changes.

In consequence of this rise of the zero, it is usual for thermometer-makers to keep the tubes of standard thermometers for a year or more before graduating them. It is obviously necessary that all thermometers used in accurate researches should be verified and recompared at their zero-points, or at parts of their scales, from time to time.

2. The second kind of movement of the zero is a temporary fall when the thermometer has been much heated, and a temporary rise when much cooled. Legrand considers that at the temperature of boiling mercury, the zero-point remounts temporarily to its position just after the thermometer was completed, but the details of his observations are not given. Despretz makes the curious remark, that every thermometer must read rather too low in summer, and too high in winter. Different thermometers are affected in very different degrees, as shown in the following observations, the thermometer-makers' names being enclosed in brackets. The degrees are Centigrade. Legrand [Bunten], 0·3° to 0·5°; Despretz, 0·23° to 0·6°; Lamont, 9 thermometers, 0·25° to 0·45°, and one, 0·62°; Forbes [Troughton], 0·3° and 0·2°, [Adie] 0·23°, [Crichton] 0·3° [Collardeau] 0·2°; Sheepshanks, average, 0·17°; Welsh, average, 0·09° to 0·11°. In making the above observations, the thermometers were boiled, and soon afterwards placed in melting ice.

The position of a thermometer, especially a very long one, when a reading is taken, is not always a matter of indifference, for at a high temperature the column of mercury may exert such a pressure as to expand the bulb slightly, and lower the reading. As thermometers are generally compared and graduated when vertical, it is obvious that the vertical reading will generally be the correct one. Professor Forbes (Phil. Trans. [1836], p. 577) detected a difference from this cause by placing the thermometer in a cylindrical vessel filled with sand, the bulb being protected from external pressure by a small stiff paper tube, and the upper part of the scale projecting out of the vessel. The whole having been very gradually raised to as high a temperature as is thought desirable, readings may be taken many times in succession, horizontally and vertically. A standard thermometer of Troughton, thus tested, gave a difference of 0·15° Fahr. If in making a standard thermometer it be known that it will have to be used both in the vertical and horizontal positions, it will be best to take the determinations of the freezing- and boiling-points in both positions.

As the mercury in a thermometer-tube is always removed some little distance from the scale to which we refer it, an obvious error, called parallax, will arise, unless the line of sight be perpendicular to the scale. With a little care, parallax may be avoided by moving the head backwards and forwards till the eye is opposite the right point. But, in making frequent or important readings, especially comparisons, it is best to use a telescope, fixed or moving at right-angles to the plane of the scale. M. Valz, of Marseilles, ingeniously proposed to plunge two-thirds of the thickness of the tube into the substance of the scale, so that the plane on which graduation is made is advanced in front of the mercurial column to the amount of one-third of the radius of the tube, in which case the error of refraction will exactly correct the error of parallax.

A light frame may easily be contrived to slide upon the scale or tube, and prevent parallax. Thus Professor Miller (Phil. Trans. [1856], cxlvi. 779), describes thermometers with arbitrary scales divided to $\frac{1}{10}$ inch, subdivided by a sliding glass scale to $\frac{1}{100}$ inch, the division of the sliding scale which is brought into apparent coincidence with the extremity of the thread of mercury being viewed through a hole in a plate of brass attached to the very light brass frame which carries the scale, so that the line of sight may be at right-angles to the axis of the tube.

Capacity and Dilatation of the Bulb.—It is necessary in certain researches to determine the coefficient of dilatation of the glass employed. This may be found, after the method of Pierre (Ann. Ch. Phys. [3], xv. 332), by constructing a thermometer of the same kind of glass, the tube being calibrated and graduated before it is filled, and the capacity of every part being ascertained by introducing mercury several times into the tube, and comparing the weight of this mercury with the number of degrees occupied. The thermometer having been completed, we easily determine, from the known capacity of its degrees, and the coefficient of dilatation of mercury, the capacity of the bulb. Taking the expansion of mercury from 32° to 212° as $\frac{1}{55{\cdot}5}$ after Dulong and Petit, we shall find k, the coefficient of dilatation of the glass from the equation:—

$$V_{32}\left(1 + \frac{1}{55{\cdot}5}\right) = V_{212}(1 + 180 \times k)$$

in which V_{32} is the actual space occupied by mercury at the temperature of 32° Fahr., and V_{212} the *apparent* volume at the temperature of boiling water.

The coefficient, Δ, of the apparent dilatation of mercury in the glass is, then, approximately for each degree Fahr.

$$\Delta = \frac{1}{55{\cdot}5 \times 180} - k.$$

The values which will thus be generally found are, for k about ·000012 for each degree Fahr; and for Δ about ·000088.

Spirit Thermometers are required for measuring temperatures which approach or sink below the freezing-point of mercury (−39° Fahr.). In their graduation we encounter the difficulty that the increments of volume of alcohol for equal increments of temperature, cannot be assumed equal, as in the case of mercury. Welsh, however (*Op. cit.* p. 315), shows how to deduce a law of expansion, by which an approximately correct scale may be graduated.

Alcohol is also used in many register thermometers; but it is an objection to such that the spirit often distils over from the end of the column, collecting in the other parts of the tube, leading an observer who is not very vigilant into error.

Register Thermometers are mercurial or spirit instruments furnished with a small index sliding in the tube, which for this purpose must have a large bore, and therefore also a large bulb. The figures (811 to 816) will sufficiently exhibit the various registering contrivances. In *fig.* 811, *a* is a small piece of steel wire, and *b* the end of the mercurial column, which forces it forward, and then leaves it at the maximum point. The tube must remain nearly horizontal, and the steel index is moved back by means of a small magnet. The chief defect of this maximum thermometer is, that a quantity of air must be left in the tube, to prevent the mercury flowing about; and the mercury in time becoming foul, the whole is thrown out of order. In *fig.* 812 the index is of wire, covered with enamel, and is *within* the column of a spirit thermometer, the end of which column carries it back by force of adhesion, but does not carry it forward. It thus gives a minimum temperature. This thermometer works very well, but is open to all the objections against a spirit thermometer. The above two instruments are known as Rutherford's, and have till lately been generally used.

Fig. 811.

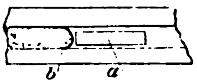
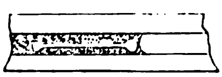
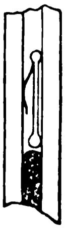


Fig. 812.



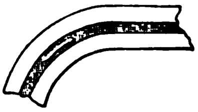
Six's Maximum and Minimum Thermometer consists of a large bulb full of alcohol joined to a tube in the form of an inverted syphon, in the lower part of which lies a short column of mercury. The extreme point reached either way by the mercury, as it is moved by the expansions and contractions of the alcohol, is marked by a small enamelled wire index sliding in the leg of the bent tube (*fig.* 813), but secured against falling from its own weight by a small spring. This instrument is very convenient for many purposes, but cannot be rendered very accurate or sure.

Fig. 813.



The Mercurial Maximum Thermometer of Negretti and Zambra seems to be the best yet invented. In this the tube is horizontal, and but little wide in bore than that of an ordinary thermometer. The bulb is bent downwards, and at the bend, the bore of the tube is nearly stopped up with an enamelled plug (*fig.* 814), which prevents the mercury from running back, as the temperature falls, provided the tube remains nearly level. The maximum reading is thus given by the end of the mercurial column remaining in the tube, and the instrument is reset, simply by inclining it until the mercury runs back and fills the bulb.

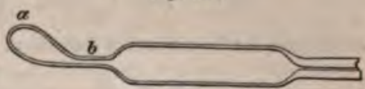
Fig. 814.



The Mercurial Minimum Thermometer, invented by Casella, is a highly ingenious instrument. The bulb is provided with a small overflow-chamber, into which the mercury freely expands during a rise of temperature. When the temperature falls again, the mercury is still retained in the chamber by adhesion to a flat surface of glass provided for the purpose. The minimum reading at the end of any period is given by the extremity of the mercurial column in the stem of the instrument. To reset the thermometer, it is inclined until all the mercury runs out of the overflow-chamber.

A very similar instrument has been devised by Negretti and Zambra. The bulb is shown in *fig.* 815, in which *a* is the overflow-chamber, and the mercury is retained in it, after once entering, by adhesion to a platinum-plug, which nearly stops up the narrow communication at *b*. These instruments are so recently invented that their relative excellence is yet unknown, but they are far superior to any of the old spirit thermometers. It is not necessary here to describe a form of mercurial minimum thermometer patented by Negretti and Zambra several years since. Although ingenious, it is a large costly instrument, open to several important objections.

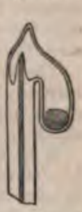
Fig. 815.



The indications of a registering thermometer can never be quite so accurate as those of an ordinary instrument. The usual process of comparison is scarcely applicable to many such thermometers, and Sir J. Herschel directs us to record the errors thus determined, but not to apply them.

The maximum thermometer of Walferdin is well adapted for taking the temperature of the sea, or of hot springs. It consists of an ordinary tube-thermometer, the upper end of which is furnished with an overflow-bulb (*fig.* 816). A corresponding but less satisfactory minimum thermometer, containing alcohol instead of mercury, is also described. (Pouillet, *Élémens de Physique*, 7me ed. tome ii. p. 689; Compt. rend. xxxviii. 770.)

Fig. 816.



A number of maximum and minimum thermometers, suited for taking the temperature of the sea, are described by Aimé. (Ann. Ch. Phys. [3], xv. 1.)

Temperature of the Air.—To place a thermometer, so that it shall accurately show the temperature of the atmosphere, is an exceedingly difficult problem. It must be shielded from radiant heat of the sun, sky, and earth's surface; also from nocturnal radiation, from rain, and the influence of any large neighbouring masses of matter, and yet must be freely exposed to the air. Meteorologists have devised various kinds of screens (Drew, *Practical Meteorology*, pp. 79—81). The difficulty might always be quite overcome, however, by placing the thermometers (*Dry and Wet Bulb*, see HYGROMETER, iii. 227), in a bright metal tube or case, and drawing a constant stream of air through it mechanically, a method tried by Welsh. (Phil. Trans. [1853], cxliii. 313.) W. S. J.

THERMOMETRIC ANALYSIS. This term is applied to certain approximative methods of quantitative analysis, depending on the observation of the temperature at which a phenomenon takes place, or of the changes of temperature accompanying chemical reactions. The following examples will be sufficient to illustrate the nature of these methods:—

1. The temperature at which a salt begins to crystallise from solution varies with the quantity of salt dissolved: hence, by observing the temperature at which crystallisation begins, the quantity of salt present in a given quantity of the solution may be inferred. This method is applied in Austria for the purpose of testing the purity of saltpetre. A known weight of the ammoniacal salt is dissolved in a certain quantity of water, and the temperature at which it begins to crystallise from the solution is compared with a table containing the crystallising temperatures of solutions of pure nitrate of potassium of various strengths. (See NITRATES, iv. 102.)

2. Many salts, in dissolving in water, produce a depression of temperature, the amount of refrigeration being different for each salt. Hence, when this amount is known for two pure salts, the proportions of them present in a mixture may be found from the fall of temperature which takes place in the solution of that mixture. This method has been applied by Gay-Lussac (Ann. Ch. Phys. [2], xii. 14; xxxix. 356) to mixtures of the chlorides of potassium and sodium.

This particular application is based upon the observation that 50 grms. of chloride of potassium, on being dissolved in 200 grms. of water, contained in a glass vessel whose weight is 185 grms. and capacity 300 cubic centimetres, produce a fall of temperature amounting to 11·4° C., while the same quantity of chloride of sodium, dissolved under exactly similar circumstances, lowers the temperature only 1·9° C.

Now let a mixture of the two salts, weighing 50 grms., be dissolved in water under exactly the same conditions; and let x be the quantity of chloride of potassium therein contained, and consequently $50-x$ the quantity of chloride of sodium. Then the fall of temperature produced by the x parts of chloride of potassium is $\frac{11·4}{50}x$, and that produced by the $50-x$ grms. of chloride of sodium is $\frac{1·9}{50}(50-x)$. The observed depression of temperature (t) is the sum of these quantities; hence the equation:

$$\frac{11·4}{50}x + \frac{1·9}{50}(50-x) = t,$$

which gives, for the amount of chloride of potassium in the mixture:

$$x = 50 \cdot \frac{t - 1·9}{11·4 - 1·9} = \frac{50\,t - 95°.}{9·5}$$

To obtain good results, it is necessary to use a delicate thermometer, capable of indicating tenths of a degree; to pulverise the mixture very finely, and accelerate the solution by shaking the flask, holding it only by the neck in so doing, in order that as little extraneous heat as possible may be communicated by the hand; and, lastly, to observe exactly the preceding stipulations as to the weights of the salt and the water, and the weight and size of the vessel. The original temperature of the water has likewise some influence on the result. Gay-Lussac used water of 20·4° C. With these precautions, the method may be depended upon for giving results of sufficient accuracy for manufacturing purposes—as, for example, in testing samples of commercial chloride of potassium used for the preparation of alum or of saltpetre. To minute scientific accuracy it has of course no pretensions.

The same method may be applied to other mixtures of salts which depress the temperature in dissolving, and likewise to such as raise it. It is more exact in proportion as the amounts of depression produced by the two salts differ more widely from one another.

3. Fixed oils (*e.g.*, olive-, poppy-, and rape-oil) evolve different degrees of heat when treated with strong sulphuric acid, and the temperatures thus produced may be applied, in like manner, to determine the proportions of two of them existing in a mixture, especially when one is a drying and the other a non-drying oil. According to Maumené (Compt. rend. xxxv. 572), 50 grms. olive-oil mixed with 10 cub. cent. sulphuric acid of 60° Baumé, become heated from 25° to 67°, that is 42°; and 50 grms. poppy-oil similarly treated are heated from 26° to 100°, or 74°.

According to Faisst and Knauss (Dingl. polyt. J. cxxxix. 53), 15 grms. of different fixed oils mixed with 5 grms. strong sulphuric acid (freed from excess of water by boiling) exhibited the following degrees of heating:

Olive-oil	from 16°—54°,	therefore	38°.
Almond-oil	„ 12°—52°	„	40°.
Rape-oil	„ 14°—69°	„	55°.
Poppy-oil	„ 17°—87°	„	70°.

With linseed-oil the rise of temperature was more than 100°, but not constant, because decomposition took place at the same time. When 15 grms. of oil were treated with 7·5 grms. of sulphuric acid containing 90 per cent. H^2SO^4, the following rises of temperature were observed:

Olive-oil	from 12°—40°,	therefore	28°
Rape-oil	„ 17°—54°	„	37°
Linseed-oil	„ 16°—91°	„	75°;

mixtures of olive-oil and poppy-oil, and of linseed-oil and rape-oil or palm-oil, exhibiting a rise of temperature nearly equal to the means of the numbers given by the individual oils. This method might therefore be applied, in default of a better, for examining mixtures of fixed oils; it requires, however, that the process be always conducted in the same way, and especially that the glasses used shall be of the same size and thickness. It would be necessary also to ascertain whether the same oil, linseed-oil for example, exhibits the same rise of temperature, when recently expressed, as when old, and under other conditions.

THERMO-MULTIPLIER. A thermo-electric pile connected with a delicate galvanometer for indicating slight changes of temperature by the thermo-electric currents produced on exposing one end of the pile to a source of heat or cold. (ELECTRICITY, ii. 413.)

THERMONATRITE. Monohydrated carbonate of sodium, $Na^2CO^3.H^2O$. (See CARBONATES, i. 795.)

THERMOPHYLLITE. A mineral occurring at Hopoovaara, in Finland, in grains or rounded indistinct crystals, cleaving easily in one direction, white to yellowish-brown, soft, of specific gravity 2·56 (Hermann). When heated, it exfoliates, and swells up to a greater bulk, but melts only on the thin edges. It is decomposed, but with difficulty, by sulphuric acid.

Analyses: *a*. By Arppe (Analyser af. finska min. p. 27).—*b*. By Hermann (J. pr. Chim. lxxiii. 213).—*c*. By Northcote (*ibid.* lxxvi. 253):

	SiO^2.	Al^2O^3.	FeO.	MgO.	K^2O.	Na^2O.	H^2O.	SnO^2. *a*.CuO.		
a.	41·20	1·71	1·20	39·58	3·19	0·46	10·84	1·00	=	99·18
b.	43·12	4·91	1·79	34·87	. .	1·33	13·14	. .	=	99·16
c.	41·48	5·49	1·59	37·42	. .	2·84	10·88	. .	=	99·70

According to the first analysis, the mineral consists essentially of $2(3MgO.2SiO^2).3H^2O$; that is to say, it differs from serpentine only in its amount of water. The second analysis leads nearly to the formula $6MgO.5SiO^2.5H^2O$, and the third to $4MgO.3SiO^2.2H^2O$. According to this last formula, the mineral is related to hydrophite and gymnite.

THERMOSTAT. An apparatus serving to maintain a body at a constant temperature. Contrivances of this sort were invented by Ure, in which two rods of different metals soldered together, being bent by change of temperature, were made to act upon a valve or stopcock, so as to regulate the draught of a furnace, the rate of escape of steam, or the influx of cold water into a boiler. (See *Ure's Dictionary of Arts*, &c., iii. 880; also Handw. d. Chem. viii. 129.)

THERYTHRIN. One of the products obtained, according to Zeise, by the simultaneous action of ammonia and sulphur upon acetone.

THIACETIC ACID. $C^2H^4OS = \left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S.$ *Sulphydrate of Acetyl.* (Kekulé, Ann. Ch. Pharm. xc. 311.—Ulrich, *ibid.* cix. 272.—Kekulé and Linnemann, ibid. cxxiii. 273.)—This acid, discovered by Kekulé in 1854, is related to acetic acid in the same manner as mercaptan to alcohol, or sulphydric acid to water. It is produced: 1. By the action of trisulphide or pentasulphide of phosphorus on glacial acetic acid, in which case the typical oxygen of the acetic acid is replaced by sulphur:

$$3\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O + P^2S^3 = P^2O^3 + 3\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}S.$$

2. By the action of acetic chloride on sulphydrate of potassium, in which case the acetyl takes the place of the potassium:

$$C^2H^3OCl + KHS = KCl + C^2H^3O.H.S.$$

3. By the action of water or alkalis on disulphide of acetyl (Kekulé and Linnemann).—4. By the action of nascent hydrogen on sulphacetylic chloride (Vizet, Ann. Ch. Pharm. cxix. 142):

$$C^2H^3ClSO^4 + 4H^2 = C^2H^4OS + HCl + 3H^2O.$$

Preparation.—300 grms. pentasulphide of phosphorus and 108 grms. glacial acetic acid are heated in a retort as nearly as possible half-filled with the mixture, till reaction commences; and the portion of the product driven over by the heat resulting from the action is collected apart. 650 grms. acetic acid and 1,800 grms. pentasulphide of phosphorus, thus treated, yield, after one rectification of the product, 250 grms. of pure thiacetic acid. (Kekulé and Linnemann.)

Properties.—Thiacetic acid is a colourless liquid, which becomes yellow by keeping, has an unpleasant odour like that of acetic and sulphydric acids together, boils at 95°, and dissolves in *alcohol* and *ether*. It is decomposed by strong *nitric acid* at a gentle heat and by the fuming acid, even in the cold, with explosion.—With *pentachloride of phosphorus* it yields chloride of acetyl and sulphochloride of phosphorus:

$$C^2H^3O.H.S + PCl^5 = C^2H^3OCl + HCl + PSCl^3.$$

Thiacetates.—Thiacetic acid is monobasic, the general formula of its salts being C^2H^3MOS for monatomic, and $C^4H^6M''O^2S^2$ for diatomic metals. Most of the thiacetates dissolve easily in water and in alcohol, and may be obtained by dissolving an oxide or carbonate in thiacetic acid, or by decomposing the barium-salt with soluble sulphates. The lead-salt, which is but slightly soluble in water, is obtained by precipitation. Thiacetic acid dissolves potassium, with evolution of hydrogen;

also zinc when heated therewith. Thiacetates are decomposed by iodine, with formation of metallic iodide and acetic disulphide (Kekulé and Linnemann):

$$2C^2H^3MOS + I^2 = 2MI + (C^2H^3O)^2S^2.$$

The *potassium-salt*, C^2H^3NaOS, the *sodium-salt*, $C^2H^3NaOS.\frac{1}{2}H^2O$, the *barium-salt*, $C^4H^6Ba''S^2O^2.3H^2O$, the *strontium-salt*, $C^4H^6Sr''S^2O^2.2H^2O$, and the *calcium-salt*, $C^4H^6Ca''S^2O^2.2H^2O$, are crystallisable (Ulrich).—The *lead-salt*, $C^4H^6Pb''O^2S^2$, obtained by precipitating acetate of lead with thiacetic acid, crystallises from hot water or alcohol, in colourless silky needles. It is very unstable, decomposing quickly, both in the dry state and in solution, with separation of lead-sulphide (Kekulé). The *mercuric salt* is obtained, by double decomposition with mercuric chloride and potassic thiacetate, as a white precipitate which soon turns black.—The *silver-* and *copper-salts* are still more unstable.—Recently precipitated *ferric hydrate* dissolves in thiacetic acid, forming a greenish solution, which deposits sulphide of iron when warmed.

Ethylic thiacetate, $C^4H^8OS = \left.\begin{matrix} C^2H^3O \\ C^2H^5 \end{matrix}\right\} S$. Obtained by the action of phosphoric pentachloride on ethylic acetate. It is a liquid lighter than water, and insoluble therein; smells like ethylic acetate and sulphydric acid. Boils at about 80°. (Kekulé.)

THIACETIC ANHYDRIDE. $(C^2H^3O)^2S$. *Acetic Monosulphide* or *Protosulphide*. (Kekulé, *loc. cit.*)—Produced by the action of phosphoric pentasulphide on acetic anhydride. On gently heating the mixture, a violent reaction takes place, and thiacetic anhydride distils over. When purified by redistillation, it forms a colourless liquid, having a peculiar odour, and boiling at 121°. It sinks in water at first, without decomposition, but afterwards decomposes, yielding acetic and sulphydric acids.

Acetic Disulphide, $(C^2H^3O)^2S^2$. (Kekulé and Linnemann, *loc. cit.*)—Produced by the action of iodine on metallic thiacetates (p. 771). Iodine is gradually added to the slightly acidulated solution of a thiacetate, till the liquid becomes brown, and the excess of iodine is removed by adding a little more of the thiacetate. Acetic disulphide then separates as a yellow liquid, which may be purified by washing with cold water, drying over chloride of calcium, filtering, and leaving it in a cold place, whereupon it solidifies in the crystalline state. The last trace of admixed sulphur may be removed by dissolving the crystals in the smallest possible quantity of carbonic disulphide, and mixing the well-cooled solution with a small additional quantity of solid acetic disulphide; the liquid then gradually deposits the pure compound in large, colourless, well-defined crystals.

Pure acetic disulphide melts at 20°; it has a peculiar, slightly hepatic odour, is insoluble in *water*, but dissolves readily in *alcohol*, *ether*, and *carbonic disulphide*. By *water* it is decomposed, gradually in the cold, quickly at the boiling heat, into sulphur and thiacetic acid; with *alkalis* the same decomposition takes place immediately. It is violently attacked by strong *nitric acid*; with more dilute nitric acid, it yields sulphuric and acetic acids. When distilled, it gives off thiacetic acid at 93°; afterwards, at 160°, a dark-coloured distillate resembling the last portion of liquid obtained in the rectification of thiacetic acid. Acetic disulphide is decomposed by mercury, even at temperatures below 100°, but the removal of the sulphur is not complete.

THIALDINE. $C^6H^{13}NS^2 = N\left\{\begin{matrix} C^2H^4.SH \\ C^2H^4.SH. \\ C^2H^3 \end{matrix}\right.$ (Wöhler and Liebig [1847], Ann. Ch. Pharm. lxi. 1.—Hofmann, *ibid.* ciii. 93.—Brusewitz and Cathander, Bull. Soc. Chim. [1867], i. 450.—Schiff, Laboratory, i. 404.)—An organic base obtained by the action of sulphydric acid on an aqueous solution of aldehydate of ammonium:

$$3C^2H^3(NH^4)O + 3H^2S = C^6H^{13}NS^2 + (NH^4)^2S + 3H^2O.$$

To prepare it, aldehydate of ammonium, free from ether and alcohol, is dissolved in 12 to 16 pts. of water; 10 or 15 drops of ammonia are added to every 30 grms. of the solution; and a gentle current of sulphydric acid gas is passed through the mixture, which then becomes milky in about half an hour, and deposits thialdine in large crystals, having the appearance of camphor; in four or five hours, it the liquid becomes clear again, and the operation is finished. The crystals are collected on a filter, washed with cold water, dried, and dissolved in ether mixed with a third of its volume of alcohol, which, when left to evaporate, deposits thialdine in rhombic tables often half an inch in diameter.—Sometimes this process yields no crystals, but a colourless fetid oil, consisting for the most part of thialdine kept in the liquid state by an oily body. To obtain the thialdine from this liquid, it is shaken up with half its volume of ether in a stoppered bottle, and then mixed with hydrochloric acid, whereupon the mixture solidifies to a crystalline mass of hydrochlorate of thialdine, which is to be washed with ether, to remove the last portions of oil, then dried, moistened with a little ammonia, and redissolved in ether.

Thialdine is likewise obtained by passing ammonia-gas into the compound of acetyl-mercaptan with sulphydric acid (i. 107):

$$C^{12}H^{26}S^7 + 8NH^3 = 2C^6H^{13}NS^2 + 3(NH^4)^2S.$$

Thialdine forms large, strongly refracting crystals, having the form of gypsum, and a density of 1·191 at 18°. It has an aromatic odour, becoming disagreeable after a while; melts at 43°, and volatilises without residue at ordinary temperatures. When distilled with water, it passes over without alteration; but when distilled alone, it decomposes, giving off a fetid oil, which partly concretes, after a while, into a brown syrupy residue containing sulphur.

Thialdine is very slightly soluble in *water*, but dissolves very easily in *alcohol* and *ether*. It does not act on vegetable colours, but dissolves easily in *acids*.

An alcoholic solution of thialdine is not immediately precipitated by *acetate of lead*, but, after some time, a yellow precipitate is formed, which changes to red, and ultimately to black.—*Nitrate of silver* forms a white precipitate, changing to yellow and black; *mercuric chloride* a white precipitate, changing to yellow; *platinic chloride* gradually forms a dingy yellow precipitate.

Thialdine and its salts, heated with a solution of *silver-nitrate*, are decomposed, with formation of silver-sulphide. Thialdine calcined with *calcic hydrate*, yields an oily alkali having the characters of chinoline. It is quickly decomposed by chloric acid. According to Gössmann, thialdine treated with *silver-oxide* and *water*, is converted into the analogous compound, leucine, $C^{12}H^{13}NO^2$; but Hofmann has shown that in this reaction, the whole of the nitrogen in the thialdine is converted into ammonia, acetic acid being formed at the same time.

Salts of Thialdine.—Thialdine unites with acids, forming soluble and crystallisable salts. The acid salts decompose when dried in a vacuum over oil of vitriol, the sides of the vessel becoming covered with slender needles, perhaps consisting of allylic sulphide, formed according to the equation, $C^6H^{13}NS^2 - NH^3 = 2C^3H^5S$. (Brusewitz and Cathander.)

Hydriodate of Thialdine, $C^6H^{13}NS^2.HI$, separates in small prisms or laminæ, on mixing the solutions of potassium-iodide and thialdine-sulphate. It is slightly soluble in cold water, but dissolves easily in boiling water, alcohol, and ether.—The *hydrobromate*, $C^6H^{13}NS^2.HBr$, crystallises in rhomboïdal prisms, resembling the hydriodate (Brusewitz and Cathander).—The *hydrochlorate*, $C^6H^{13}NS^2.HCl$, obtained by dissolving thialdine in hydrochloric acid, crystallises in fine, colourless, highly lustrous prisms, moderately soluble in cold water, less soluble in alcohol, insoluble in ether, decomposed by heat (Wöhler and Liebig).—The *hydrocyanate* is formed on adding cyanide of potassium in sufficient quantity to sulphate of thialdine, partly as a white precipitate, partly as an oil which floats on the surface of the liquid; the precipitate and the oil gradually form into crystals, which may be purified by recrystallisation from ether. (Brusewitz and Cathander.)

The *nitrate*, $C^6H^{13}NS^2.HNO^3$, is easily obtained by agitating the ethereal solution of crude thialdine with moderately strong nitric acid, the mixture solidifying to a crystalline pulp, which may be purified by recrystallisation. It forms colourless needles, more soluble in water than the hydrochlorate, soluble in alcohol, insoluble in ether. (Wöhler and Liebig.)

The *oxalate*, probably an acid salt, separates from a solution of thialdine in oxalic acid, in large quadrangular prisms, which are easily decomposed by evaporation. (Brusewitz and Cathander.)

The *acid phosphate*, $C^6H^{13}NS^2.H^3PO^4$, is obtained like the sulphate, and its solution is decomposed by heat nearly in the same manner. It crystallises in slender needles, very soluble in water, alcohol, and ether, and melting at a high temperature. Phosphate of sodium, added to a solution of sulphate of thialdine, throws down a white precipitate, consisting of free thialdine. (Brusewitz and Cathander.)

Acid sulphate, $C^6H^{13}NS^2.H^2SO^4$.—A solution of thialdine in excess of sulphuric acid, is decomposed by heat, yielding a number of products, among which are sulphate of thialdine and needle-shaped crystals, probably consisting of sulphide of allyl (*supra*). The solution, evaporated in a dry vacuum, yields the acid sulphate in large prisms, soluble in water, alcohol, and ether. When sulphocyanate of potassium is added to the solution of this salt, a precipitate is formed, and a gas is given off, not consisting either of carbonic anhydride or of sulphydric acid. (Brusewitz and Cathander.)

Tartrate of thialdine crystallises in large prisms.

Derivatives and Analogues of Thialdine.

Ethyl-thialdine, $C^8H^{17}NS^2 = C^6H^{12}(C^2H^5)NS^2$.—Obtained, though not in the pure state, by saturating aldehyde with ethylamine, and treating the syrupy liquid with sulphydric acid; it then separates as a neutral, easily decomposible oil. (Flückiger, Jahresb. 1856, p. 519.)

Methyl-thialdine, $C^6H^{12}(CH^3)NS^2$, is obtained in a similar manner, by the action of sulphydric acid on aldehydate of methylamine. (Flückiger.)

Methyl-thialdammonium, $C^7H^{16}NS^2$.—Thialdine unites directly with iodide of methyl (mixed with an equal volume of ether), forming the compound $C^6H^{13}NS^2.CH^3I = C^7H^{16}NS^2.I$, which solidifies in a crystalline mass. This compound, when purified by washing with ether, and recrystallisation (avoiding a boiling heat), behaves like iodide of tetramethylammonium. It is insoluble in ether, soluble in alcohol, somewhat soluble in water, and is precipitated therefrom, without decomposition, by cold caustic potash; by boiling potash, however, it is completely decomposed, forming a brown resinous substance, smelling of aldehyde, which is likewise produced when thialdine is strongly heated with iodide of methyl. The acid-reacting aqueous solution of the iodide, treated with recently precipitated silver-oxide, becomes alkaline, and gives a precipitate of silver-iodide; but quickly undergoes complete decomposition, yielding silver-sulphide, aldehyde, ammonia, and hydrate of tetramethylammonium:

$$4C^7H^{16}NS^2I + 10Ag^2O + 3H^2O = 4AgI + 8Ag^2S + 12C^2H^4O + 3NH^3 + \left.\begin{matrix}N(CH^3)^4\\H\end{matrix}\right\}O$$

From its behaviour with iodide of methyl, Hofmann infers that thialdine is a nitrile base, $N(C^6H^{12}S^2)'''$. But, from recent experiments by Schiff (the details of which are not yet published), it appears most probable that thialdine, and its homologues and analogues, may be represented by the general formula $N\left\{\begin{matrix}C^nH^{2n}.SH\\C^nH^{2n}.SH.\\C^nH^{2n-1}\end{matrix}\right.$ By the action of ammonium-sulphide on acrylic and œnanthic aldehydes, Schiff has obtained acrothialdine, $C^9H^{13}NS^2 = N\left\{\begin{matrix}C^3H^4.SH\\C^3H^4.SH,\\C^3H^3\end{matrix}\right.$ and œnanthothialdine, $C^{21}H^{43}NS^2 = \left\{\begin{matrix}C^7H^{14}.SH\\C^7H^{14}.SH.\\C^7H^{13}\end{matrix}\right.$

THIAMETHALDINE. Syn. with METHYL-THIALDINE.

THIANISOIC ACID. $C^{10}H^{14}SO^4 = C^{10}H^{12}O.H^2SO^3$. (Städeler and Wächter, Ann. Ch. Pharm. cxvi. 163.)—An acid containing the elements of anethol or anise-camphor (i. 297) and sulphurous acid, and (according to Städeler and Wächter) identical with Limpricht and Ritter's anisoic acid (i. 305). To prepare it, anethol is boiled with nitric acid of specific gravity 1·1; the oil thereby produced (together with oxalic and a small quantity of anisic acid) is rectified; and the distillate, which passes over between 215° and 245°, is left for some time in contact with a concentrated solution of acid sodium-sulphite and a small quantity of alcohol; the sodium-salt of thianisoic acid then crystallises out.

The pure acid is separated from the barium-salt by addition of sulphuric acid, and remains in the crystalline form, when the filtered solution is left to evaporate. It has a strongly acid and astringent taste, with sweet aftertaste, dissolves easily in water, alcohol, and ether; its dilute solution may be boiled without decomposition.

The crystals, which contain $C^{10}H^{14}SO^4.2H^2O$, melt below 200°, and the acid, if not more strongly heated, solidifies again in the crystalline form on cooling; but on raising the temperature to 100°, the water of crystallisation is given off, and the acid then solidifies in the amorphous state on cooling. At a stronger heat, it blackens and decomposes, giving off sulphurous anhydride, with an odour somewhat like that of anise, but of a fetid character.

Thianisoates.—Thianisoic acid is monobasic, and mostly forms crystallisable salts, easily soluble in water, sparingly soluble in alcohol, insoluble in ether.

The *ammonium-salt* forms crystals resembling those of the sodium-salt, and containing 1 at. water.

The *barium-salt*, $C^{20}H^{26}Ba''S^2O^8.3H^2O$, separates on mixing the concentrated solution of the sodium-salt with barium-chloride, in delicate laminæ, and crystallises from a hot aqueous solution in beautiful stellate groups; it may be recrystallised, without alteration, from hot hydrochloric acid. It dissolves in 12 pts. of cold water. The crystals give off 2 at. water at 103°, and the remainder at 130°.—The *calcium-salt*, $C^{20}H^{26}Ca''S^2O^8.2H^2O$, separates from a mixture of the concentrated solution of the sodium-salt with chloride of calcium, in shining needles, which dissolve in water more readily than the barium-salt, and are moderately soluble in warm alcohol.

The *cupric salt* crystallises from a mixture of the sodium-salt with cupric sulphate, in black shining laminæ.

The *lead-salt* crystallises from a solution of the sodium-salt, mixed with neutral acetate of lead, in thick well-defined tables and prisms.—A *basic lead-salt* separates, as a white amorphous precipitate, on mixing the sodium-salt with basic acetate of lead.

The *magnesium-salt*, $C^{20}H^{26}Mg''S^2O^8.5H^2O$, is likewise obtained by double decomposition, and crystallises in rectangular tables, moderately soluble in water and in alcohol. They give off 3 at. water at 100°, and the remaining 2 at. at 130°.

The *silver-salt* forms delicate prismatic laminæ, moderately soluble in water, and not decomposed by boiling water.

The *sodium-salt*, $C^{10}H^{13}SO^4.H^2O$, prepared as above described, crystallises in warty groups of shining laminæ, or in thin rhombic tables. It dissolves in 6·5 pts. water at mean temperature, sparingly in cold, easily in boiling alcohol. The crystals are slightly efflorescent, and give off their water at 100°.

THIANISOL. C^8H^8SO. *Hydride of Sulphanisyl.*—A white pulverulent substance, formed by the action of ammonium-sulphide on anishydramide (i. 299).

THIERSCHITE. The name applied by Liebig to a deposit of calcic oxalate found on some parts of the Parthenon at Athens. (See OXALATES, iv. 254.)

THIETHALDINE. Syn. with ETHYL-THIALDINE (p. 773).

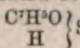
THIET-SIE. A resinous substance used as a varnish by the Burmese. It exudes from a tree in the form of a light-brown, very viscid liquid, of the consistence of treacle, but on exposure to the air for a few minutes, becomes quite black, and hard on the surface. The same change takes place instantly in contact with caustic potash. The resin spread in a thin layer, on wood or other solid bodies, quickly forms a hard deep-black coating of great brilliancy.

On digesting the unaltered substance with alcohol of 80 per cent. at a gentle heat, the greater part gradually dissolves; and on decanting the clear liquid from the insoluble residue, and distilling off the alcohol, there remains a very tenacious gummy residue of a rich brown colour, which undergoes no change of colour on exposure to the air, but very slowly hardens. In contact with caustic potash, however, it blackens like the original substance.

The residue, insoluble in alcohol, dissolves for the most part in ordinary ether, forming a dark-brown solution, and leaving a light-brown solid resin. The ethereal solution, when evaporated, leaves a residue which, on exposure to the air, instantly becomes quite black, and after a short time nearly solid. This then is the portion of the original substance to which the property of blackening on exposure to the air is due.

The solid resin, insoluble in alcohol and ether, which forms but a small part of the original substance, is quite unalterable in the air. When heated with nitric acid, it yields a crystalline sublimable acid, exhibiting the characters of succinic acid. (H. Watts, *Unpublished Experiments.*)

THIOBENZALDINE. Syn. with HYDRIDE OF SULPHAZOBENZOYL (p. 481).

THIOBENZOIC ACID. C^7H^6OS = 
$\left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}S$. (Cloez, Ann. Ch. Pharm. cxv. 27.)—This acid, analogous to thiacetic acid, is produced by mixing an alcoholic solution of potassium-monosulphide with chloride of benzoyl till the liquid no longer blackens lead-paper. A brisk action then takes place, chloride of potassium is deposited, and thiobenzoate of potassium remains in solution, together with ethylic sulphide, ethylic benzoate, and other products. On distilling off the alcohol over the water-bath, and mixing the aqueous solution of the residue with dilute hydrochloric acid, an oily liquid separates, which smells of mercaptan, and, when left to stand in a cool place, deposits thiobenzoic acid in colourless crystals.

Thiobenzoic acid, when purified by recrystallisation from carbonic disulphide, forms small rhombic tables, inodorous and tasteless. It melts at 120°, becomes rose-coloured and gives off sulphydric acid between 160° and 180°, and decomposes further at 300°, yielding an oily distillate which solidifies on cooling. The acid is quite insoluble in water, slightly soluble in alcohol and ether, easily soluble in mercaptan, ethylic sulphide, and carbonic disulphide. It dissolves without decomposition in alcoholic potash, soda, or ammonia, and forms definite salts with bases. The alkaline thiobenzoates precipitate *ferric salts.* —The *lead-salt* is a white precipitate.—*Ethylic thiobenzoate* appears to be contained in the oily liquid from which the acid is deposited in the course of preparation above described.

THIOBENZOL, or **THIOBENZOYL-HYDRIDE.** See DERIVATIVES OF BENZOYL-HYDRIDE (i. 571).

with sulphydric acid; it then separates as a neutral, easily decomposible oil. (**Flückiger**, Jahresb. 1856, p. 519.)

Methyl-thialdine, $C^6H^{12}(CH^3)NS^2$, is obtained in a similar manner, by the action of sulphydric acid on aldehydate of methylamine. (**Flückiger.**)

Methyl-thialdammonium, $C^7H^{16}NS^2$.—Thialdine unites directly with iodide of methyl (mixed with an equal volume of ether), forming the compound $C^6H^{13}NS^2.CH^3I = C^7H^{16}NS^2.I$, which solidifies in a crystalline mass. This compound, when purified by washing with ether, and recrystallisation (avoiding a boiling heat), behaves like iodide of tetramethylammonium. It is insoluble in ether, soluble in alcohol, somewhat soluble in water, and is precipitated therefrom, without decomposition, by cold caustic potash; by boiling potash, however, it is completely decomposed, forming a brown resinous substance, smelling of aldehyde, which is likewise produced when thialdine is strongly heated with iodide of methyl. The acid-reacting aqueous solution of the iodide, treated with recently precipitated silver-oxide, becomes alkaline, and gives a precipitate of silver-iodide; but quickly undergoes complete decomposition, yielding silver-sulphide, aldehyde, ammonia, and hydrate of tetramethylammonium:

$$4C^7H^{16}NS^2I + 10Ag^2O + 3H^2O = 4AgI + 8Ag^2S + 12C^2H^4O + 3NH^3 + \left.\begin{array}{r}N(CH^3)^4\\ H\end{array}\right\}O$$

From its behaviour with iodide of methyl, Hofmann infers that thialdine is a nitrile base, $N(C^6H^{13}S^2)'''$. But, from recent experiments by Schiff (the details of which are not yet published), it appears most probable that thialdine, and its homologues and analogues, may be represented by the general formula $N\left\{\begin{array}{l}C^nH^{2n}.SH\\ C^nH^{2n}.SH.\\ C^nH^{2n-1}\end{array}\right.$ By the action of ammonium-sulphide on acrylic and œnanthic aldehydes, Schiff has obtained **acrothialdine**, $C^9H^{15}NS^2 = N\left\{\begin{array}{l}C^3H^4.SH\\ C^3H^4.SH,\\ C^3H^5\end{array}\right.$ and **œnanthothialdine**, $C^{21}H^{43}NS^2 = \left\{\begin{array}{l}C^7H^{14}.SH\\ C^7H^{14}.SH.\\ C^7H^{13}\end{array}\right.$

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THIANISOIC ACID. $C^{10}H^{14}SO^4 = C^{10}H^{12}O.H^2SO^3$. (**Städeler** and **Wächter**, Ann. Ch. Pharm. cxvi. 163.)—An acid containing the elements of anethol or anise-camphor (i. 297) and sulphurous acid, and (according to **Städeler** and **Wächter**) identical with Limpricht and Ritter's anisoic acid (i. 305). To prepare it, anethol is boiled with nitric acid of specific gravity 1·1; the oil thereby produced (together with oxalic and a small quantity of anisic acid) is rectified; and the distillate, which passes over between 215° and 245°, is left for some time in contact with a concentrated solution of acid sodium-sulphite and a small quantity of alcohol; the sodium-salt of thianisoic acid then crystallises out.

The pure acid is separated from the barium-salt by addition of sulphuric acid, and remains in the crystalline form, when the filtered solution is left to evaporate. It has a strongly acid and astringent taste, with sweet aftertaste, dissolves easily in water, alcohol, and ether; its dilute solution may be boiled without decomposition.

The crystals, which contain $C^{10}H^{14}SO^4.2H^2O$, melt below 200°, and the acid, if not more strongly heated, solidifies again in the crystalline form on cooling; but on raising the temperature to 100°, the water of crystallisation is given off, and the acid then solidifies in the amorphous state on cooling. At a stronger heat, it blackens and decomposes, giving off sulphurous anhydride, with an odour somewhat like that of anise, but of a fetid character.

Thianisoates.—Thianisoic acid is monobasic, and mostly forms crystallisable salts, easily soluble in water, sparingly soluble in alcohol, insoluble in ether.

The *ammonium-salt* forms crystals resembling those of the sodium-salt, and containing 1 at. water.

The *barium-salt*, $C^{20}H^{26}Ba''S^2O^8.3H^2O$, separates on mixing the concentrated solution of the sodium-salt with barium-chloride, in delicate laminæ, and crystallises from a hot aqueous solution in beautiful stellate groups; it may be recrystallised, without alteration, from hot hydrochloric acid. It dissolves in 12 pts. of cold water. The crystals give off 2 at. water at 103°, and the remainder at 130°.—The *calcium-salt*, $C^{20}H^{26}Ca''S^2O^8.2H^2O$, separates from a mixture of the concentrated solution of the sodium-salt with chloride of calcium, in shining needles, which dissolve in water more readily than the barium-salt, and are moderately soluble in warm alcohol.

The *cupric salt* crystallises from a mixture of the sodium-salt with cupric sulphate, in black shining laminæ.

The *lead-salt* crystallises from a solution of the sodium-salt, mixed with neutral acetate of lead, in thick well-defined tables and prisms.—A *basic lead-salt* separates, as a white amorphous precipitate, on mixing the sodium-salt with basic acetate of lead.

The *magnesium-salt*, $C^{20}H^{26}Mg''S^2O^8.5H^2O$, is likewise obtained by double decomposition, and crystallises in rectangular tables, moderately soluble in water and in alcohol. They give off 3 at. water at 100°, and the remaining 2 at. at 130°.

The *silver-salt* forms delicate prismatic laminæ, moderately soluble in water, and not decomposed by boiling water.

The *sodium-salt*, $C^{10}H^{13}SO^4.H^2O$, prepared as above described, crystallises in warty groups of shining laminæ, or in thin rhombic tables. It dissolves in 6·5 pts. water at mean temperature, sparingly in cold, easily in boiling alcohol. The crystals are slightly efflorescent, and give off their water at 100°.

THIANISOL. C^8H^8SO. *Hydride of Sulphanisyl.*—A white pulverulent substance, formed by the action of ammonium-sulphide on anishydramide (i. 299).

THIERSCHITE. The name applied by Liebig to a deposit of calcic oxalate found on some parts of the Parthenon at Athens. (See OXALATES, iv. 254.)

THIETHALDINE. Syn. with ETHYL-THIALDINE (p. 773).

THIET-SIE. A resinous substance used as a varnish by the Burmese. It exudes from a tree in the form of a light-brown, very viscid liquid, of the consistence of treacle, but on exposure to the air for a few minutes, becomes quite black, and hard on the surface. The same change takes place instantly in contact with caustic potash. The resin spread in a thin layer, on wood or other solid bodies, quickly forms a hard deep-black coating of great brilliancy.

On digesting the unaltered substance with alcohol of 80 per cent. at a gentle heat, the greater part gradually dissolves; and on decanting the clear liquid from the insoluble residue, and distilling off the alcohol, there remains a very tenacious gummy residue of a rich brown colour, which undergoes no change of colour on exposure to the air, but very slowly hardens. In contact with caustic potash, however, it blackens like the original substance.

The residue, insoluble in alcohol, dissolves for the most part in ordinary ether, forming a dark-brown solution, and leaving a light-brown solid resin. The ethereal solution, when evaporated, leaves a residue which, on exposure to the air, instantly becomes quite black, and after a short time nearly solid. This then is the portion of the original substance to which the property of blackening on exposure to the air is due.

The solid resin, insoluble in alcohol and ether, which forms but a small part of the original substance, is quite unalterable in the air. When heated with nitric acid, it yields a crystalline sublimable acid, exhibiting the characters of succinic acid. (H. Watts, *Unpublished Experiments.*)

THIOBENZALDINE. Syn. with HYDRIDE OF SULPHAZOBENZOYL (p. 481).

THIOBENZOIC ACID. $C^7H^6OS = \left.\begin{matrix}C^7H^5O\\H\end{matrix}\right\}S$. (Cloez, Ann. Ch. Pharm. cxv. 27.)—This acid, analogous to thiacetic acid, is produced by mixing an alcoholic solution of potassium-monosulphide with chloride of benzoyl till the liquid no longer blackens lead-paper. A brisk action then takes place, chloride of potassium is deposited, and thiobenzoate of potassium remains in solution, together with ethylic sulphide, ethylic benzoate, and other products. On distilling off the alcohol over the water-bath, and mixing the aqueous solution of the residue with dilute hydrochloric acid, an oily liquid separates, which smells of mercaptan, and, when left to stand in a cool place, deposits thiobenzoic acid in colourless crystals.

Thiobenzoic acid, when purified by recrystallisation from carbonic disulphide, forms small rhombic tables, inodorous and tasteless. It melts at 120°, becomes rose-coloured and gives off sulphydric acid between 160° and 180°, and decomposes further at 300°, yielding an oily distillate which solidifies on cooling. The acid is quite insoluble in water, slightly soluble in alcohol and ether, easily soluble in mercaptan, ethylic sulphide, and carbonic disulphide. It dissolves without decomposition in alcoholic potash, soda, or ammonia, and forms definite salts with bases. The alkaline thiobenzoates precipitate *ferric salts*.—The *lead-salt* is a white precipitate.—*Ethylic thiobenzoate* appears to be contained in the oily liquid from which the acid is deposited in the course of preparation above described.

THIOBENZOL, or **THIOBENZOYL-HYDRIDE.** See DERIVATIVES OF BENZOYL-HYDRIDE (i. 571).

THIOBUTYRIC ACID. C^4H^8OS.—An acid homologous with thiacetic acid, produced by the action of phosphoric protosulphide on butyric acid (i. 694).

THIOCAPRINALDINE. A compound, analogous to thialdine, formed, according to Wagner (Pharm. Centr. 1861, p. 32), by the action of sulphydric acid on the ammonia-compound of capric or rutic aldehyde (i. 742).

THIOCHRONIC ACID. A product of the action of sulphurous acid on tetrachloroquinone (p. 29).

THIOCINNOL. C^9H^8S.—A pulverulent substance formed, together with sulphide of ammonium, by the action of sulphydric acid on hydrocinnamide (Cahours, Compt. rend. xxv. 458):

$$C^{27}H^{24}N^2 + 4H^2S = 3C^9H^8S + (NH^4)^2S.$$

THIOCUMOL, or **THIOCUMINOL.** $C^{10}H^{12}S$.—A body produced from cuminol (cuminic aldehyde, $C^{10}H^{12}O$) by the action of ammonium-sulphide (ii. 183).

THIOCYANIDES, or *Hydrothiocyanates.*—Salts formed by boiling persulphocyanogen with alkalis. (See PERSULPHOCYANOGEN, iv. 381.)

THIODIACETIC ACID. See THIODIGLYCOLLIC ACID.

THIODIGLYCOLLAMIC ACID, $C^4H^7NSO^3 = \left.\begin{matrix}H^2\\(C^2H^2O)''\\(C^2H^2O)''\\H\end{matrix}\right\}\begin{matrix}N\\O\\S\end{matrix}$, or *Thiodiacetamic Acid,* $\left.\begin{matrix}H^2\\(C^4H^4SO^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (E. Schulze, Zeitschr. f. Chem. 1866, p. 181; Jahresb. 1865, p. 345.)—The *barium-salt* of this acid, $C^8H^{12}Ba''N^2S^2O^6.H^2O$, produced by treating thiodiglycollimide with cold baryta-water, crystallises, by evaporation over sulphuric acid, in needles, or forms a gummy mass if quickly dried. The acid, $C^4H^7NSO^3$, separated from the barium-salt by sulphuric acid, or obtained by heating the acid ammonium-salt for several days to 145°, crystallises in colourless prisms, permanent in the air, melting at 125°, and converted at higher temperatures into thiodiglycollimide. It dissolves slowly in cold, easily in boiling water, forming an acid solution which is not precipitated by lead- or silver-salts.—The *calcium-salt*, $C^8H^{12}Ca''N^2S^2O^6.H^2O$, crystallises from a syrupy solution in small needles.—The *silver-salt*, $C^4H^6AgNSO^3$, may be crystallised from hot water.

THIODIGLYCOLLAMIDE, $C^4H^8N^2SO^2 = \left.\begin{matrix}(C^2H^2O)''\\(C^2H^2O)''\\H^4\end{matrix}\right\}\begin{matrix}N^2\\S\end{matrix}$, or *Thiodiacetodiamide,* $\left.\begin{matrix}(C^4H^4SO^2)''\\H^4\end{matrix}\right\}N^2$. (Schulze, *loc. cit.*)—This compound is obtained by the action of neutral sulphide of ammonium on chloracetamide in alcoholic solution. The reaction, which consists in the substitution of 1 at. S for 2 at. Cl in a double molecule of chloracetamide, seems to show that the second of the above formulæ is the more correct expression of the composition of the product:

$$\underbrace{\left.\begin{matrix}C^4H^4Cl^2O^2\\H^2\end{matrix}\right\}N^2}_{\text{2 mol. chloracetamide.}} + (NH^4)^2S = 2NH^4Cl + \underbrace{\left.\begin{matrix}(C^4H^4SO^2)''\\H^2\end{matrix}\right\}N^2}_{\text{Thiodiacetodiamide.}}.$$

The product, after washing with alcohol and recrystallisation from water, forms small, white, quadratic octahedrons, which melt when heated, and then decompose, giving off the odour of ammonium-sulphide.

THIODIGLYCOLLIC or **THIODIACETIC ACID.** $C^4H^6SO^4 = \left.\begin{matrix}C^2H^2O\\C^2H^2O\\H^2\end{matrix}\right\}\begin{matrix}S\\O^2\end{matrix}$ or $\left.\begin{matrix}(C^4H^4SO^2)''\\H^2\end{matrix}\right\}O^2$. (Schulze, Zeitschr. f. Chem. 1865, p. 73; 1866, p. 181; Jahresb. 1864, p. 325; 1865, p. 345.—Wislicenus, Zeitschr. f. Chem. 1865, p. 621; Jahresb. 1865, p. 344.)—This acid, which has the composition of diglycollic acid (ii. 912), with 1 at. oxygen replaced by sulphur, or of a double molecule of acetic acid ($C^4H^8O^4$) in which 2 at. hydrogen are replaced by 1 at. sulphur, is produced: 1. By boiling thiodiglycollamide with baryta-water as long as ammonia is evolved:

$$C^4H^8N^2SO^2 + 2H^2O = 2NH^3 + C^4H^6SO^4.$$

By precipitating the solution of the resulting barium-salt with acetate of lead, decomposing the lead-salt with sulphydric acid, and evaporating the filtrate, thiodiglycollic acid is obtained in crystals. (Schulze.)

2. Ethylic thiodiglycollate, $C^4H^4(C^2H^5)^2SO^4$, is produced by the action of potassium-sulphydrate on ethylic chloracetate:

$$2C^2H^2(C^2H^5)ClO^2 + KHS = C^4H^4(C^2H^5)^2SO^4 + KCl + HCl.$$

This ether, treated with alcoholic potash, yields thiodiglycollate of potassium, which may be converted into a lead- or silver-salt by precipitation, and from this the acid may be obtained. (Wislicenus.)

Thiodiglycollic acid crystallises in large, thin, rhombic plates (Schulze). It melts at 129° (Schulze), at 126° (Wislicenus), volatilises completely when cautiously heated, dissolves in 2·37 pts. of water at 18°, and is soluble in alcohol. The aqueous solution is precipitated by lead- and silver-salts. The acid is not attacked by fuming hydrochloric acid, even at 150°—180°; but when heated to 150°, with excess of *hydriodic acid* (boiling at 125°), it is reduced to acetic acid:

$$C^4H^6SO^4 + 4HI = 2C^2H^4O^2 + H^2S + 2I^2.$$

The thiodiglycollates are mostly soluble in water, insoluble in alcohol, and easily crystallisable.—The *acid ammonium-salt*, obtained by treating monochloracetate of ammonium with alcoholic sulphide (? sulphydrate) of ammonium, crystallises in octahedral forms, mostly prismatically distorted. When heated to 180°—200°, it gives off water and ammonia, and leaves thiodiglycollimide, $C^4H^5NSO^2$ (Schulze).—The *neutral potassium-salt* crystallises in broad colourless prisms, which give off 1 at. water at 120° (Schulze). Wislicenus, by the action of alcoholic potash on ethylic thiodiglycollate, obtained it in thin needles, containing $C^4H^4K^2SO^4.H^2O$.—The *acid potassium-salt* is anhydrous, permanent in the air, and less soluble than the neutral salt. (Schulze.)

The *barium-salt*, $C^4H^4Ba''SO^4$, in the anhydrous state, forms sparingly soluble crystalline crusts. By leaving it for some time in contact with the mother-liquor, a hydrated salt, $C^4H^4Ba''SO^4.5H^2O$, is obtained in prismatic crystals, which are permanent in the air, but become opaque and anhydrous when immersed in hot water. (Schulze.)

The *cupric salt*, $C^4H^4Cu''SO^4.H^2O$, is formed, on mixing moderately concentrated solutions of the ammonium-salt and cupric sulphate, as a bluish-white crystalline precipitate, which, on heating the liquid, is converted into blue crystals of the anhydrous salt. (Schulze.)

The *neutral lead-salt*, $C^4H^4Pb''SO^4$, is crystalline, soluble in hot water and in dilute nitric acid.—A *basic lead-salt*, $C^4H^4Pb''SO^4.Pb''O$, is formed when the ammonium-salt is mixed with basic lead-acetate at the boiling heat.—The *silver-salt* is a flocculent precipitate.—The *zinc-salt* crystallises with 4 at. water in sparingly soluble rhombic plates.

Ethylic Thiodiglycollate, $C^4H^4(C^2H^5)^2SO^4$, is obtained:—1. By saturating the alcoholic solution of the acid with hydrochloric acid (Schulze).—2. Together with other products, by the action of potassium-sulphydrate on ethylic monochloracetate. On treating the product of this reaction with water, a fetid oil is separated, which, when rectified, yields ethylic thiodiglycollate between 267° and 268° (Wislicenus). This ether is a colourless liquid, which has a faint ethereal odour, is insoluble in water, distils, for the most part undecomposed, at 240°—250°, and, when treated with alcoholic ammonia, yields thiodiglycollamide. (Schulze.)

THIODIGLYCOLLIC CHLORIDE. Thiodiglycollic acid, treated with pentachloride of phosphorus, forms a colourless chloride, difficult to purify, which yields with alcohol a sulphuretted oil, insoluble in water, and apparently not identical with ethylic thiodiglycollate, inasmuch as it is decomposed by ammonia, with formation of ammonium-sulphide. (Schulze.)

THIODIGLYCOLLIC ETHER. Syn. with ETHYLIC THIODIGLYCOLLATE (*vid. sup.*).

THIODIGLYCOLLIMIDE, $C^4H^5NSO^2 = \left.\begin{matrix}(C^2H^2)''\\(C^2H^2O)''\\H\end{matrix}\right\}\begin{matrix}N\\S\end{matrix}$, or **THIODIACETIMIDE,** $\left.\begin{matrix}(C^4H^4SO^2)''\\H\end{matrix}\right\}N$, is formed by the dehydration of acid thiodiglycollate of ammonium, and is deposited from a hot aqueous solution, decolorised by animal charcoal, in thin prismatic needles or laminæ. It is sparingly soluble in cold water, melts at 128°, and sublimes undecomposed at a higher temperature. On mixing its slightly ammoniacal solution with nitrate of silver, argento-thiodiglycollimide, $C^4H^4AgNSO^2$, is precipitated in white flocks, which are decomposed by boiling.—By *baryta-water*, at the boiling heat, the imide is converted, with evolution of ammonia, into thiodiglycollate of barium; in cold baryta-water, on the other hand, it dissolves as thiodiglycollamate of barium (p. 776). (Schulze.)

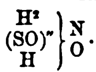
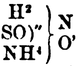
THIOFORMIC ACID. A compound, probably homologous with thiacetic acid, produced in small quantity by the action of sulphydric acid on formate of lead, at 200°—300°. It forms small transparent crystals, which have an alliaceous odour, are insoluble in water, may be recrystallised from alcohol, melt at 120°, and sublime at a lower temperature. They are insoluble in sulphide of ammonium, and dissolve but slightly in boiling potash-ley. Their alcoholic solution, which does not redden litmus, forms with acetate of lead a yellowish, and with silver-salts a whitish precipitate, both of which are blackened and decomposed by heat. (Limpricht, Ann. Ch. Pharm. xcvii. 361.)

THIOFUCUSOL. A body analogous and very similar to thiofurfurol, produced by treating fucusol in alcoholic solution with sulphydric acid. By dry distillation, it yields a product of decomposition called pyrofucusol, which crystallises in needles, and has probably the same composition as pyrofurfurol, $C^8H^6O^2$. (Stenhouse, Ann. Ch. Pharm. lxxiv. 293.)

THIOFURFOL, or **THIOFURFUROL.** C^5H^4OS.—A compound formed by the action of ammonium-sulphide on furfurol, or of sulphydric acid on furfuramide dissolved in alcohol. (See FURFUROL, ii. 753.)

THIOMELANIC ACID. The black mass produced by heating alcohol with excess of sulphuric acid. It was formerly supposed to consist of carbon, but, according to Erdmann (J. pr. Chem. xxi. 291), it is a sulphuretted acid, capable of forming salts with potash and other bases. It has not been obtained in a sufficiently definite state to enable its composition to be determined with accuracy, and is probably a mixture. (See *Gmelin's Handbook*, viii. 240.)

THIOMETHALDINE. Syn. with METHYL-THIALDINE (p. 774).

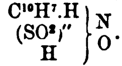
THIONAMIC ACID.  $NH^3SO^2 = \left.\begin{matrix}H^2\\(SO)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. *Sulfit-ammon.*—This acid, which differs from acid sulphite of ammonium ($NH^4.H.SO^3$) by the want of 1 at. water, is produced by the action of dry ammonia-gas on an excess of sulphurous anhydride. It is a crystalline volatile substance, of a yellowish colour (perhaps due to impurity), and very soluble in water. In the moist state, or in solution, it quickly undergoes a complete decomposition into sulphate of ammonium, trithionate of ammonium, and other products. When sulphurous anhydride is mixed with excess of dry ammonia-gas, two volumes of the former unite with four volumes of the latter, forming thionamate of ammonium,  $\left.\begin{matrix}H^2\\(SO)''\\NH^4\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$, which is an amorphous, volatile, neutral, deliquescent salt, speedily decomposing in solution. (H. Rose, Pogg. Ann. xxxiii. 275; xlii. 425; Gm. ii. 455.)

THIONAMIDE. $N^2H^4(SO)''$.—Produced by the action of sulphurous chloride on dry ammonia:

$$4NH^3 + SOCl^2 = 2NH^4Cl + N^2H^4SO.$$

The sulphurous chloride should be well cooled, and the ammonia-gas passed in slowly. The product is a white, pulverulent, non-crystalline solid, from which the sal-ammoniac may be extracted by cold water. Thionamide is converted by hot water into neutral sulphite of ammonium, from which it differs by 2 at. water: $(NH^4)^2SO^3 - 2H^2O = N^2H^4SO$. It is instantly decomposed by alkalis with evolution of ammonia, and by acids with evolution of sulphurous anhydride. (Schiff, Ann. Ch. Pharm. cii. 111.)

THIONAPHTHALIC ACID. Syn. with NAPHTHYLSULPHUROUS ACID. (See SULPHUROUS ETHERS, p. 560.)

THIONAPHTHAMIC ACID, more properly, **NAPHTHYLSULPHAMIC ACID,** $C^{10}H^9NSO^3$ =  $\left.\begin{matrix}C^{10}H^7.H\\(SO^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (Piria, Ann. Ch. Phys. [3], xxxi. 217.)—This acid is produced, together with naphthionic acid, with which it is isomeric, by the action of ammonium-sulphite on nitronaphthalene. The orange-yellow crystals obtained in the preparation of naphthionic acid (iv. 17), consist of naphthylsulphamate of ammonium. The acid has not been obtained in the free state; on attempting to decompose a thionaphthamate with an acid, even with acetic acid, it is resolved into naphthylamine and sulphuric acid.

The naphthylsulphamates are generally prepared by double decomposition from the ammonium-salt. They are all soluble, and resemble each other in appearance and colour. They usually crystallise in large nacreous laminæ of an amethyst or reddish colour.

They undergo decomposition by exposure to the air, their solutions becoming reddish-brown. Heat and light assist this decomposition, while the presence of alkalis confers stability on the solutions. Distilled with lime in excess, the naphthylsulphamates yield naphthylamine in the form of an oil which crystallises on cooling.

The *ammonium-salt* is obtained in crystals by dissolving the crude salt, prepared as above described, in 2 pts. of boiling water containing a few drops of ammonia, and cooling the solution. It forms small, reddish, nacreous laminæ, the solution of which becomes more rapidly coloured than those of the other salts. It dissolves very easily in water, and in alcohol. When its perfectly neutral solution is heated between 80° and 90°, the water being replaced as it evaporates, it becomes coloured, and strongly acid, deposits a brown resin, and yields sulphate of naphthylamine.

The *potassium-salt*, $C^{10}H^8KNSO^3$, is obtained by boiling the ammonium-salt with excess of potassium-carbonate, till it ceases to evolve ammonia. On cooling, large nacreous laminæ crystallise out, resembling boric acid. The salt is very soluble in water, but only slightly soluble in alcohol, and in aqueous potash or carbonate of potassium.—The *sodium-salt*, $C^{10}H^8NaSO^3$, prepared in like manner, forms reddish laminæ, easily soluble in hot, but sparingly in cold water, especially in presence of sodium-carbonate.

The *barium-salt*, $C^{20}H^{16}Ba''N^2S^2O^6.6H^2O$ (?), is prepared by double decomposition with chloride of barium and naphthionate of potassium. — The *calcium-salt*, $C^{20}H^{16}Ca''N^2S^2O^6$, and the *magnesium-salt*, $C^{20}H^{16}Mg'N^2S^2O^6$, are very soluble.

The *lead-salt*, $C^{20}H^{16}Pb''N^2S^2O^6$, is prepared by decomposing a boiling solution of the potassium-salt with nitrate of lead, taking care that the potassium-salt is in excess. When the nitrate of lead is in excess, a double salt is produced, which appears to contain equal numbers of atoms of thionaphthamate and nitrate of lead. The thionaphthamate of lead is deposited from its boiling solution in crystalline grains, which may be purified by a second crystallisation. It then forms a light, crystalline, reddish powder, very slightly soluble in water, and almost insoluble in alcohol.

Acetato-thionaphthamate of lead, $C^4H^6Pb''O^4.C^{20}H^{16}Pb''N^2S^2O^6$.—When concentrated and nearly boiling solutions of potassium-thionaphthamate and lead-acetate are mixed, the latter being in excess and acidified with acetic acid, there is deposited on cooling a double salt, crystallising in reddish micaceous laminæ grouped around a common centre. It is very slightly soluble in cold, more soluble in hot water.

THIONESSAL, $C^{26}H^{18}S$. *Schwefelessal. Schwefelesyl.* (Laurent, Ann. Ch. Phys. [3], i. 292).—A compound produced, together with stilbene, by the dry distillation of thiobenzol:

$$\underset{\text{Thiobenzol.}}{8C^7H^6S} = \underset{\text{Thionessal.}}{C^{26}H^{18}S} + \underset{\text{Stilbene.}}{2C^{14}H^{12}} + 2CS^2 + 3H^2S.$$

It is obtained, from the portion of the distillate insoluble in ether, by solution in petroleum, and crystallises from the hot solution in silky needles. It is very sparingly soluble in alcohol and ether, more soluble in petroleum. It melts at 178°, often remains liquid till cooled down to the ordinary temperature of the air, and then solidifies without assuming a crystalline structure. When heated to 233°, it crystallises as soon as a crystal is thrown into the liquid mass. It is decomposed by potassium, with formation of potassium-sulphide. Alcoholic potash-solution does not decompose it, even at the boiling heat. By boiling *nitric acid*, it is slowly converted into a yellow crust of tetranitrothionessal, $C^{26}H^{14}(NO^2)^4S$.—*Bromine* attacks it violently, forming a solid mass of tetrabromothionessal, $C^{26}H^{14}Br^4S$, insoluble in alcohol, ether, and petroleum.

THIONURIC ACID. *Alloxanosulphurous acid* (Laurent). $C^4H^5N^3SO^6$. (Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 268, 314, 331.)—An acid formed by the simultaneous action of ammonia and sulphurous acid on alloxan (i. 137). It is obtained by decomposing its lead-salt with sulphuretted hydrogen, and evaporating the filtrate at a gentle heat. It forms a crystalline mass, consisting of fine needles: it is permanent in the air, reddens litmus strongly, and has a very sour taste. It is readily soluble in water; when the solution is boiled, it is decomposed into dialuramide, which separates out, and sulphuric acid:

$$C^4H^5N^3SO^6 + H^2O = C^4H^5N^3O^3 + H^2SO^4.$$

It is a dibasic acid.

The *normal ammonium-salt*, $C^4H^3(NH^4)^2N^3SO^6.H^2O$, is obtained by boiling for some time a mixture of aqueous alloxan and sulphurous acid, saturated with ammonia; or a mixture of aqueous sulphite and carbonate of ammonium, and alloxan; the salt crystallises, on cooling, in four-sided tables, which lose 6 per cent. (1 at.) water at 100°, assuming a rose-colour. It is slightly soluble in cold, readily in hot water; the solution reduces metallic silver from nitrate of silver, in the specular form. When fused with solid potash, it yields sulphite of potassium. Mineral acids decompose it at a boiling heat (not in the cold), into dialuramide and sulphuric acid. By prolonged heating to 200°, it is for the most part resolved into sulphate of ammonium and xanthinine, $C^4H^3N^3O^2$ (Finck, Ann. Ch. Pharm. cxxxii. 298):

$$C^4H^3(NH^4)^2N^3SO^6 = (NH^4)^2SO^4 + C^4H^3N^3O^2.$$

The *acid ammonium-salt*, $[C^4H^4(NH^4)N^3SO^6]$, is obtained in fine white needles, by evaporating in a water-bath an aqueous solution of the normal salt with a small quantity of sulphuric acid: if the sulphuric acid is in excess, dialuramide, uramilic acid, and finally dialuric acid, is formed. The aqueous solution of this salt is decomposed by boiling into sulphate of ammonium and dialuric acid:

$$C^4H^8N^4SO^6 + 2H^2O = \underset{\text{Dialuric acid.}}{C^4H^4N^2O^4} + (NH^4)^2SO^4.$$

The *barium-salt* is obtained as a flocculent precipitate, which gradually becomes crystalline, when the ammonium-salt is added to chloride of barium. It is readily soluble in hydrochloric acid; boiled with nitric acid, it yields sulphate of barium, but no free sulphuric acid.

The *lead-salt* is obtained by adding thionurate of ammonium to neutral acetate of lead. It is a gelatinous precipitate, which, on cooling, aggregates into tufts of white or rose-coloured needles. By dry distillation, it yields urea, and another crystalline product.

With sulphate of copper, thionurate of ammonium gives a yellowish-brown precipitate, whith is probably a cuprous salt.

Gregory (Compt. chim. 1845, p. 118) mentions a peculiar acid, containing the elements of thionuric acid minus ammonia. F. T. C.

THIONYL. SO.—The radicle of the sulphurous compounds: *e.g.*, sulphurous chloride, $(SO)''Cl^2$ = chloride of thionyl (p. 542).

THIONYLAMIC ACID. Syn. with THIONAMIC ACID (p. 778).

THIONYLAMIDE. Syn. with THIONAMIDE (p. 778).

THIOPHOSPHAMIC ACID. $PH^4NSO^2 = \left.\begin{matrix}H^2\\(PS)'''\\H^2\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix} = P(NH^2)H^2SO^2.$

Sulphoxyphosphamic Acid. (Gladstone and Holmes, Chem. Soc. J. xviii. 7.)—This acid is formed by the action of aqueous ammonia on sulphochloride of phosphorus. (Respecting the mode of formation of this and the following acid, see iv. 606.) The sulphochloride added to strong aqueous ammonia diluted with an equal bulk of water, dissolves slowly on agitation, and forms an acid liquid containing sal-ammoniac and thiophosphamic acid. The latter has not been isolated, but its neutralised solution yields, with solutions of heavy metallic salts, a series of salts resembling the thiophosphodiamates (*infra*), and represented by the formula $PNH^2M''SO^2$. No precipitates are obtained with solutions of nickel, cobalt, iron, aluminium, barium, calcium, or magnesium. A solution of potassio-stannous chloride forms a white bulky precipitate, soluble in hydrochloric acid. Mercuric chloride throws down yellow mercuric sulphochloride, which, in presence of excess of thiophosphamic acid, turns black—a reaction which may serve to distinguish this acid from the following.

THIOPHOSPHODIAMIC ACID. $PH^5N^2SO = \left.\begin{matrix}H^4\\(PS)'''\\H\end{matrix}\right\}\begin{matrix}N^2\\O\end{matrix} = P(NH^2)^2HSO.$

Sulphoxyphosphodiamic Acid. (Gladstone and Holmes, *loc. cit.*)—A monobasic acid formed, together with sal-ammoniac, by the action of ammonia-gas, or of the strongest aqueous solution of ammonia, on sulphochloride of phosphorus. The sulphochloride takes up about 4 at. ammonia (40 per cent. of its weight), and is converted into a white mass, easily soluble in water, and forming an acid solution, which, when neutralised, yields thiophosphodiamates, $P(NH^2)^2M''SO$ and $P^2(NH^2)^4M''S^2O^2$, by double decomposition. These salts decompose when heated, giving off ammonia and sulphide of ammonium.—The *cupric salt*, $P^2N^4H^8Cu''S^2O^2$, is a yellowish-white precipitate, insoluble in dilute hydrochloric acid and in ammonia, soluble in cyanide of potassium, and turning brown when heated.—The *zinc-salt*, $P^2N^4H^8Zn''S^2O^2$, is a white flocculent precipitate, easily soluble in dilute acids and in ammonia.—The *cadmium-salt*, $P^2N^4H^8Cd''S^2O^2$, exhibits similar properties.—The *lead-salt* is obtained, on adding chloride of lead to the neutralised solution of the acid, as a white precipitate, soluble in dilute nitric acid, and turning black when heated with water.—The *silver-salt* was obtained, mixed with silver-chloride, as a white precipitate, insoluble in dilute nitric acid, turning black in presence of excess of silver.—*Stannous chloride* and *mercuric chloride* form white precipitates, the latter of which quickly passes into the yellow compound, $HgS.HgCl^2$, but is not under any circumstances converted into black sulphide of mercury—a character which distinguishes thiophosphodiamic from thiophosphamic acid. The filtered solution contains an acid not yet examined.—*Cobalt-salts* give a bluish-white, *nickel-salts* a greenish-white precipitate, both of which are soluble in dilute acids and in ammonia.—*Barium-, calcium-, magnesium-, aluminium-,* and *ferric salts* give no precipitate. On attempting to isolate the acid from its silver- or copper-salt, a liquid was obtained, which, when evaporated over oil of vitriol, decomposed with separation of sulphur.

THIOSALICOL. C^7H^6OS. *Sulphosalicylic Hydride.*—A compound produced by the action of sulphydric acid on hydrosalicylamide (iii. 218).

THIOSINAMINE. $C^4H^8N^2S = N^2\left\{\begin{matrix}(CS)'' \\ C^3H^5 \\ H^3\end{matrix}\right.$ *Allyl-sulphocarbamide. Rhodalline.*—This compound is formed by the union of the elements of 1 at. allylic sulphocyanate with 1 at. ammonia, just as allyl-carbamide is formed by the union of ammonia and allylic cyanate. It was discovered, in 1834, by Dumas and Pelouze (Ann. Ch. Phys. [2], liii. 181), afterwards examined by Aschoff (J. pr. Chem. iv. 314), Löwig and Weidmann (*ibid.* xix. 218), Robiquet and Bussy (*ibid.* xix. 232), and more completely by Will (Ann. Ch. Pharm. lii. 1).

Preparation.—By saturating oil of mustard with ammonia-gas, or mixing it with 3 or 4 times its bulk of strong aqueous ammonia, and leaving the mixture to stand till it is converted into a crystalline mass. If the mother-liquor filtered from these crystals be evaporated, to expel the excess of ammonia, and boiled with animal charcoal, a colourless liquid is obtained, which, on evaporation, yields crystals of pure thiosinamine to the last drop. It is best to use pure mustard-oil in the preparation, as the crude oil, when treated with ammonia, likewise forms a yellow resinous substance, which cannot be removed without loss.

Properties.—Thiosinamine, purified, if necessary, by recrystallisation, forms white shining prisms, which (according to Schabus) belong to the monoclinic system, and are cleavable parallel to $+P\infty$ and oP. It is inodorous, but has a bitter taste. Melts at 70·6° (Dumas and Pelouze), at 74° (Wertheim), forming a colourless liquid, which cannot be volatilised without decomposition. In moderate doses, it does not exert a poisonous action on the human organism, but nevertheless produces sleeplessness, palpitation of the heart, &c. (Wöhler and Frerichs, Ann. Ch. Pharm. lxv. 342). It is neutral to vegetable colours, but nevertheless exhibits some of the characters of ammonia, especially in the facility with which it dissolves oxide and chloride of silver. It dissolves in hot much more readily than in cold water, and is easily soluble in alcohol and ether.

Thiosinamine exhibits the same properties, whether prepared from natural or from artificial mustard-oil.

Decompositions.—1. Thiosinamine is completely decomposed at high temperatures, sulphocyanic acid and other volatile products being formed, and charcoal remaining behind.—2. By *electrolysis*, it yields sulphurous and hydrocyanic acids, and a yellow sulphuretted organic compound, which is deposited at the negative pole (Schlagdenhauffen, J. Pharm. [3], xliv. 100).—3. *Chlorine* decomposes it in aqueous solution, forming large quantities of hydrochloric and sulphuric, but no sulphocyanic acid (Aschoff).—4. *Bromine* (according to Aschoff) forms a white precipitate with thiosinamine; but, according to Maly (Bull. Soc. Chim. [1867], ii. 129), this takes place only when the thiosinamine is impure. An alcoholic solution of pure thiosinamine dissolves bromine, without elimination of hydrobromic acid, and the solution yields, by evaporation, crystals of hydrobromate of bromothiosinamine.—5. *Iodine* added in sufficient quantity to aqueous thiosinamine separates a brown oil; the watery liquid then exhibits acid reaction, and when boiled deposits a white substance containing iodine and sulphur.—6. Dilute *phosphoric* and *sulphuric acids*, heated with thiosinamine, evolve sulphocyanic acid.—7. *Nitric acid* oxidises it.—8. *Potassium*, heated with it to the melting-point, decomposes it with explosion.—9. *Baryta-water* decomposes thiosinamine at the boiling heat, forming sulphide and carbonate of barium. But little ammonia is evolved, and the filtrate, when evaporated, leaves a non-crystalline and scarcely alkaline syrup, which appears to be a base different from sinamine. The other fixed alkalis act like baryta.—10. The *protoxides* of *lead* and *mercury* abstract from thiosinamine sulphur and hydrogen, a metallic sulphide and water being formed, together with sinamine:

$$\underset{\text{Thiosinamine.}}{C^4H^8N^2S} + Hg''O = \underset{\text{Sinamine.}}{C^4H^6N^2} + Hg''S + H^2O.$$

11. The aqueous solution of thiosinamine forms a white precipitate with mercuric salts, grey with mercurous salts, brownish-yellow with trichloride of gold, white with

nitrate of silver, &c. It gradually decolorises ferric chloride, and forms a flocculent precipitate on boiling. It likewise decolorises a moderately strong solution of cupric sulphate, the liquid then depositing blue flocks on addition of alcohol. When warm, it dissolves recently precipitated chloride of silver, the liquid becoming milky as it cools, and depositing a pitchy substance, containing thiosinamine and chloride of silver.

Combinations.—Thiosinamine does not form crystallisable salts with ***sulphuric, nitric,*** *acetic*, or *oxalic acid.*

The *hydrochlorate*, $C^4H^8N^2S.HCl$, is produced by passing dry hydrochloric acid gas over dry thiosinamine at a gentle heat. The product gives off vapours of hydrochloric acid when exposed to moist air. (Will.)

The *chloroplatinate*, $2(C^4H^8N^2S.HCl).PtCl^4$, is obtained by saturating thiosinamine with hydrochloric acid gas, and mixing the cold aqueous solution of the resulting hydrochlorate with platinic chloride. It is a yellowish-red precipitate, consisting of needle-shaped rhombic crystals; melts and blackens at a gentle heat, and decomposes at higher temperatures, leaving sulphide of platinum. If the liquids are mixed hot, or if the platinic chloride contains nitric acid, or if a dark-coloured solution of thiosinamine in aqueous hydrochloric acid is used, precipitates of variable composition are formed. (Will.)

A *chloromercurate*, containing $2Hg''Cl^2.C^4H^8N^2S$, or $Hg''Cl^2 + 2HCl\,.\,N^2\left\{\begin{matrix}CS''\\ C^3H^5\\ H.Hg''\end{matrix}\right.$, is obtained, as a curdy white precipitate, by mixing the aqueous solutions of mercuric chloride and hydrochlorate of thiosinamine. It is soluble in acetic acid. (Will.)

A compound of thiosinamine with nitrate of silver, $NO^3Ag.C^4H^8N^2S$, is produced, by mixing the concentrated aqueous solution of thiosinamine and nitrate of silver, as a white crystalline precipitate, which, after washing with water, and drying at 100°, forms a greenish-white mass, slightly alterable on exposure to light. Boiling water decomposes it into sulphide of silver, and other products not yet examined. Aqueous sulphydric acid converts it into thiosinamine and sulphide of silver. (Will.)

Derivatives of Thiosinamine.

Bromothiosinamine, $C^4H^7BrN^2S$. (Maly, J. pr. Chem. c. 321; Bull. Soc. Chim. [1867], ii. 129.)—The hydrobromate of this base, $C^4H^7BrN^2S.HBr$, is formed, as already observed, by the direct addition of bromine to thiosinamine in alcoholic solution, 1 at. thiosinamine taking up 2 at. bromine without evolution of hydrobromic acid. It separates, on evaporation, as a crystalline mass, soluble in water and in alcohol. It melts at 146°—147°, and at a higher temperature gives off vapours having the irritating odour of allyl-compounds, and leaves a very porous cinder. Its aqueous solution forms, with *nitrate of silver*, a copious precipitate of chloride of silver, and with *platinic chloride*, brilliant orange-yellow scales of the chloroplatinate, $2(C^4H^7BrN^2S.HBr).PtCl^4$.

Chloride of silver added to the aqueous solution of the hydrobromate removes half the bromine, forming bromide of silver and hydrochlorate of bromothiosinamine, $C^4H^7BrN^2S.HCl$, which is soluble in water and in alcohol, and is deposited from the aqueous solution in crystals grouped like wavellite,—from the alcoholic solution in more bulky crystals, apparently belonging to the monoclinic system. It melts at 129°—130°.—With *platinic chloride*, it forms orange-yellow shining scales of the chloroplatinate, $2(C^4H^7BrN^2S.HCl).PtCl^4$, insoluble in boiling alcohol, soluble in boiling water, and partly decomposed thereby; and with *auric chloride* a dark red-purple precipitate of a chloroaurate, together with bromide of gold.

Hydrate of bromothiosinammonium, $C^4H^8BrN^2S.H.O$.—A solution of hydrobromate of bromothiosinamine, treated with oxide of silver, yields bromide of silver and a strongly alkaline bitter liquid, which may be evaporated to a syrupy consistence; and when treated with hydrochloric acid, yields hydrochlorate of bromothiosinamine.

Amyl-thiosinamine, obtained by the direct combination of allylic sulphocyanate with amylamine, is an uncrystallisable syrup, which yields a crystalline chloroplatinate. (Hinterberger, Ann. Ch. Pharm. lxxxiii. 346.)

Ethyl-thiosinamine, $C^6H^{12}N^2S = N^2\left\{\begin{matrix}(CS)''\\ C^3H^5\\ C^2H^5\\ H^2\end{matrix}\right.$.—*Thiosinethylamine.* (Hinterberger, *loc. cit.*—Weltzien, Ann. Ch. Pharm. xciv. 103.)—Formed by the direct combination of allylic sulphocyanate or sulphocarbimide, $N(CS)''(C^3H^5)$, with ethylamine,

$N(C^2H^5)H^2$ (Hinterberger), or as a hydriodate, by the action of ethylic iodide on thiosinamine. (Weltzien.)

Oil of mustard absorbs gaseous ethylamine with considerable rise of temperature. Liquid ethylamine hisses when dropt into mustard; and on adding the oil to liquid ethylamine, it is thrown out by the violence of the action. When ethylamine was passed in excess into mustard-oil cooled with ice, a thin syrupy liquid was formed, having the odour of ethylamine, and a bitter aromatic taste. This liquid, after standing for some time, became red-brown, but did not yield crystals, or form crystallisable salts with acids; when heated, it gave off white fumes, which condensed to oily alkaline drops, exhibiting a blood-red colour with ferric chloride. (Hinterberger.)

The *hydriodate*, $C^6H^{12}N^2S.HI$, is obtained by heating thiosinamine with ethylic iodide in alcoholic solution, and evaporating, as a white, feathery, crystalline mass, resembling sal-ammoniac. It dissolves in water, alcohol, and ether, and turns yellow in the air from separation of iodine (Weltzien).—The *hydrochlorate* is obtained by decomposing the hydriodate with oxide of silver, precipitating the excess of the silver from the filtrate with hydrochloric acid, and evaporating the filtered solution. The residue is a syrupy uncrystallisable mass, soluble in water and in alcohol. (Weltzien.)

Platinum-salt, $2(C^6H^{12}N^2S.HCl).PtCl^4$.—On saturating the syrupy liquid obtained by the action of mustard-oil on ethylamine with dry hydrochloric acid gas, dissolving the resulting viscid mass in absolute alcohol, and adding an alcoholic solution of platinic chloride, yellow needle-shaped crystals of the platinum-salt quickly separated; the mother-liquor, when left to itself for some time, yielded crystals of more definite shape (Hinterberger). Weltzien's hydrochlorate mixed with chloride of platinum, yielded a yellow, easily soluble, indistinctly crystalline mass.

Methyl-thiosinamine, obtained like the ethyl-compound, is a brown uncrystallisable syrup, which yields a crystalline chloroplatinate. (Hinterberger.)

Naphthyl-thiosinamine, $C^{14}H^{14}N^2S = N^2(CS''.C^3H^5.C^{10}H^7.H^2)$. *Thiosin-naphthylamine.* (Zinin, J. pr. Chem. lvii. 173.)—This compound is produced by adding 30 pts. of mustard-oil to a solution of 43 pts. of naphthylamine in eight times that weight of 90 per cent. alcohol, and separates after awhile in crystals, grouped in small, white, radiated hemispheres, the mother-liquor yielding an additional quantity when evaporated. It is white, insoluble in water, sparingly soluble in ether and in cold alcohol, more easily in boiling alcohol. It melts at 130°, forming a clear liquid, which solidifies again in the crystalline form. By careful heating, a portion of it may be distilled without alteration.

Naphthyl-thiosinamine is decomposed by *hydrate of lead*, yielding sulphide of lead, together with a substance which crystallises from boiling alcohol in silky grains, and an unctuous substance, still more soluble in alcohol.

With *acids*, naphthyl-thiosinamine behaves like the phenyl-compound.

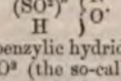
Phenyl-thiosinamine, or **Thiosinaniline,** $C^{10}H^{12}N^2S = N^2(CS''.C^3H^5.C^6H^5.H^2)$. (Zinin, *loc. cit.*)—Obtained by pouring oil of mustard into an equivalent quantity of aniline dissolved in about four times its weight of alcohol of 90 per cent. The mixture becomes hot, and, on cooling, deposits the compound in foliated crystals. If a weaker solution of aniline be used, the crystals sometimes attain the length of four millimetres, and exhibit the form of tables with four or six faces.

Thiosinaniline is colourless, transparent, destitute of taste and smell, insoluble in water, very soluble in alcohol and ether. It melts at 95°, forming a colourless liquid, which solidifies in a radiated mass on cooling. When distilled it yields an oil, which has the odour of leeks, and does not solidify. It is desulphurised by hydrate of lead, yielding a substance which is very soluble in alcohol, and crystallises in silky needles; also as an uncrystallisable resinous body.

Thiosinaniline does not show much tendency to combine with acids. It dissolves in hot concentrated hydrochloric acid, but is precipitated by water in its original state. It likewise crystallises unaltered from an alcoholic solution of sulphuric or hydrochloric acid. Heated with nitric acid, it is decomposed, forming a resinous substance.

THIOSINANILINE. Syn. with PHENYL-THIOSINAMINE (see above).

THIOSIN-NAPHTHYLAMINE. Syn. with NAPHTHYL-THIOSINAMINE (see above).



THIOTOLUIC ACID, $C^7H^9NSO^3$, more properly, **BENZYLSULPHAMIC** or **TOLYLSULPHAMIC ACID,** $\left.\begin{matrix}C^7H^7.H\\(SO^2)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$. (Hilkenkamp, Ann. Ch. Pharm. xcv. 86.)—An acid related to toluene (benzylic hydride, C^7H^8, i. 573), in the same manner as naphthylsulphamic acid, $C^{10}H^9NSO^3$ (the so-called thionaphthamic acid, p. 778), is related to naphthalene, $C^{10}H^8$. To prepare it, 60 grms. of nitrotoluene are boiled, for eight or ten hours, with 400 grms. of a concentrated solution of ammonium-sulphite, a small quantity of ammonium-carbonate, and a litre of absolute alcohol, the ammoniacal distillate being continually poured back, till the liquid assumes an acid reaction; and the cooled solution, filtered from the crystals which separate, is concentrated, with addition of ammonium-carbonate. The red solution, on cooling, deposits benzylsulphamate of ammonium, in radiate groups of slender needles, which may be rendered colourless by repeated levigation with ether. This salt is easily soluble in water and in alcohol, insoluble in ether. It is permanent in dry air, but turns red in contact with moist air. When heated it first melts, and then chars. Its aqueous solution is not perceptibly altered by acids, even at the boiling heat, and for the most part does not yield precipitates with metallic salts. Chlorine separates from it yellow oily drops, having the odour of tetrachloroquinone.

The *barium-salt*, prepared by adding the ammonium-salt to baryta-water, boiling till all the ammonia is expelled, precipitating the excess of barium by carbonic acid, and evaporating the filtrate, forms white crystalline crusts.—The *potassium-salt*, $C^7H^8KNSO^3$, obtained by boiling the ammonium-salt with carbonate of potassium, evaporating to dryness, and exhausting the residue with boiling absolute alcohol, separates from the alcoholic solution, on cooling, in small nodular groups of crystals, less soluble in water and in alcohol than the ammonium-salt.—The *sodium-salt*, prepared in like manner, forms small, white, nodular crystals, easily soluble in water, sparingly soluble in absolute alcohol.

The acid has not been obtained in the pure state. Neither does the mother-liquor of the crude ammonium-salt, when treated with hydrochloric acid, yield a compound analogous to naphthionic acid.

THIOTOLUOLIC ACID, $C^7H^9NS^2O^6$, more properly, *Benzyldisulphamic* or *Tolyldisulphamic acid*, $\left.\begin{matrix}C^7H^7\\(SO^2)^2\\H^2\end{matrix}\right\}\begin{matrix}N\\O^2\end{matrix}$, has been already described (p. 480).

THIOVALERIC ACID. The product of the action of phosphoric pentachloride on valerianic acid.

THJÖRSA LAVA. A lava from Hekla, consisting of a mixture of the true lava-mass with thjörsanite (anorthite) and chrysolite, both of which minerals occur crystallised in distinct cavities of the lava. The greyish-black lava contains silica, alumina, ferrous oxide, lime, and magnesia, as principal constituents, together with small quantities of soda and potash, and traces of manganese-, nickel-, and cobalt-oxides. (Genth.)

THJÖRSANITE. A variety of anorthite occurring in the Thjörsa lava on Hekla, in crystallo-laminar, brittle, transparent masses, of white to grey colour, and vitreous lustre, nacreous on the cleavage-surfaces. Specific gravity = 2·688 at 17°. Hardness = 6. Insoluble in hydrochloric acid. Melts before the blowpipe in thin splinters. Contains, according to Genth's analyses, 48·75 per cent. silica, 30·59 alumina, 1·50 ferric oxide, 17·22 lime, 0·97 magnesia, 1·13 soda, and 0·62 potash.

THOMAITE. A name applied by Mayor (Bergwerksfreund, viii. 6) to a quadratic variety of ferrous carbonate from the Siebengebirge.

THOMSONITE. *Mesolite* (in part). *Mesotype* (in part). *Needle Zeolite* (in part). *Comptonite. Chalilite. Tripoclase. Ozarkite.*—A hydrated silicate of aluminium, calcium, and sodium, occurring in trimetric crystals, exhibiting the combination $\infty P \,.\, \infty\bar{P}\infty \,.\, oP \,.\, 2\breve{P}\infty \,.\, \infty\breve{P}\infty$. Axes $a : b : c = 1 : 1·0117 : 0·7225$. Angle $\infty P : \infty P = 90° 40'$; $oP : \breve{P}\infty = 144° 9'$. Cleavage easy parallel to $\infty\bar{P}\infty$ and $\infty\breve{P}\infty$. The mineral likewise occurs columnar, with radiated structure, and amorphous. Hardness = 5 to 5·5. Specific gravity = 2·35 to 2·4. Lustre vitreous, inclining to pearly. Colour snow-white; brown in impure varieties. Streak uncoloured. Transparent to translucent. Fracture uneven. Brittle. Before the blowpipe it intumesces, becoming white and opaque, the edges only being rounded at a white heat. When pulverised, it gelatinises with nitric or hydrochloric acid.

Analyses:—*a.* Lochwinnock, Renfrewshire (Thomson's *Outlines*, i. 315).—*b.* Dumbarton (Berzelius, Berz. Jahresb. ii. 96).—*c.* Seeberg, near Kaaden, Bohemia: *Comptonite* (Zippe, Verh. d. Ges. d. vat. Mus. in Böhmen, 1836, p. 3).—*d.* Elbogen, Bohemia: *Comptonite* (Melly, J. pr. Chem. xiv. 511).—*e.* The Cyclopean Isles, near Catania; accompanied by analcime and mesolite (Sart. v. Waltershausen, Vulk. Gest. pp. 272, 286).—*f.* Between the Bulandstind and the Berufjörd, Iceland: pale-yellow, intergrown with scolecite; specific gravity = 2·362 (v. Waltershausen).—*g.* Magnet Cove, Arkansas: in elæolite; specific gravity = 2·24 (Smith and Brush, Sill. Am. J. [2], xvi. 41).—*h.* Dalsmypen, Faröe Islands (Retzius, Berz. Jahresb. iv. 151).—*i.* Hauenstein, in Bohemia: formerly called *mesolite*; specific gravity = 2·357 (Rammelsberg, Pogg. Ann. xlvi. 286):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Silica . .	37·68	38·30	38·25	37·00	39·27	39·86	36·85	39·20	39·63
Alumina .	31·66	30·70	32·00	31·07	29·50	31·44	29·24	30·05	31·25
Lime . .	15 25	13·54	11·96	12·60	12·38	13·33	13·95	10·58	7·27
Soda . .	. . .	4·53	6·53	6·25	4·46	6·29	3·91	8·11	8·03
Water . .	13·10	13·10	11·50	12·24	13·23	11·39	13·80	13·40	13·30
Magnesia .	0·64	. .	. .	. .	0·12				
Ferric oxide .	0·66	. .	. .	. .	1·48	. .	1·55	0·50	
	98·99	100·17	100·24	99·16	100·44	102·31	99·30	101·84	99·48

These analyses lead to the formula:

$$\left.\begin{matrix}(\mathrm{Ca}'';\mathrm{Na}^2)\mathrm{O}.\mathrm{SiO}^2\\ \mathrm{Al}^2\mathrm{O}^3.\mathrm{SiO}^2\end{matrix}\right\}.\tfrac{5}{2}\mathrm{H}^2\mathrm{O},\ \text{or}\ 2\left[\left.\begin{matrix}\mathrm{Ca}'';\mathrm{Na}^2\\ \overset{\prime\prime\prime}{\mathrm{Al}}{}^2\end{matrix}\right\}\mathrm{Si}^2\mathrm{O}^8\right].5\mathrm{H}^2\mathrm{O};$$

whence thomsonite may be regarded as consisting of 2 at. of a sodiferous anorthite with 5 at. water. The mineral from Lochwinnoch appears, from Thomson's analysis, to be a nearly pure hydrated calcio-aluminic silicate (i. 308).

Thomsonite occurs also near Kilpatrick, in Scotland. The variety called *Comptonite* is met with in the lavas of Vesuvius, as well as in the localities above mentioned. Thomson's *Scoulerite* from Portrush, in Ireland, is near thomsonite in composition, but contains less alumina and water, and 3½ per cent. soda. The varieties called *carphostilbite*, *chalilite*, *ozarkite*, and *picrothomsonite* are described in their alphabetical places.

THORINA. See THORINUM, OXIDE OF (p. 787).

THORINUM, or **THORIUM.** *Atomic Weight*, 115·72; *Symbol*, Th.—A very rare element belonging to the group of earth-metals. It was discovered in 1828 by Berzelius in thorite from Esmark, on the Norwegian island Lövön, and has since been found by Wöhler in pyrochlore, by Karsten in monazite, by Bergemann and others in the variety of thorite called orangite, by Mosander and Chydenius (Bull. Soc. Chim. 1866, ii. 433) in euxenite from Arendal, and by Bahr (Pogg. Ann. cxix. 572) in gadolinite, orthite, and a mineral resembling the latter. Bahr at first regarded the earth obtained from these three minerals as the oxide of a new metal, *wäsium*; but he has since recognised its identity with thorina. (Ann. Ch. Pharm. cxxxii. 227.)

Metallic thorinum is obtained by heating the anhydrous chloride with potassium or sodium. The decomposition takes place with slight detonation, but with scarcely visible ignition, and may therefore be performed in a glass vessel. The reduced thorinum, when freed from soluble salts, is a grey metallic powder, which may be easily pressed together, and when triturated with polished agate, acquires an iron-grey metallic lustre. Its specific gravity, according to Chydenius, is 7·657 to 7·795. When heated, it burns with great splendour, producing snow-white thorina, which exhibits not the slightest trace of fusion or aggregation. Thorinum is not oxidised by water, either hot or cold. According to Berzelius, it is but slowly attacked by nitric, sulphuric, or hydrofluoric acid, but dissolves easily in hydrochloric acid, especially when gently heated. According to Chydenius, it disolves easily in nitric, slowly in hydrochloric acid, and in sulphuric acid only when heated. It is not attacked by solutions of caustic alkalis. (Berzelius.)

THORINUM, BROMIDE OF. Obtained by dissolving thorina in hydrobromic acid; dries up to a gummy mass on evaporation; forms a double salt with bromide of potassium. (Berzelius.)

THORINUM, CHLORIDE OF. ThCl^2.—Prepared by heating an intimate mixture of thorina and charcoal in a stream of dry chlorine-gas. The decomposition takes place slowly, and the chloride of thorinum, which is not very volatile, is deposited on the cooler part of the tube, as a white crystalline sublimate; by renewed sublimation, it may be obtained in white shining crystals (Berzelius), which, according to Chydenius, are rectangular four-sided tables, having their edges bevelled by planes inclined to the basal faces at angles of 129° 7′ and 143° 8′. They deliquesce in the air, and dissolve in water with rise of temperature (Berzelius). The chloride does not volatilise at 440°. (Chydenius.)

Hydrate of thorinum dissolves easily in hydrochloric acid, and the solution, when concentrated to a certain strength—especially if it contains excess of hydrochloric acid—solidifies to a radio-crystalline mass of the hydrated chloride. The solution, evaporated to dryness, leaves a deliquescent saline mass, which gives off hydrochloric acid at a higher temperature. Chloride of thorinum is soluble in alcohol.

Ammonio-thorinic chloride, $4\mathrm{NH}^4\mathrm{Cl}.\mathrm{ThCl}^2.4\mathrm{H}^2\mathrm{O}$, is obtained by heating a dry mixture of chloride of thorinum and sal-ammoniac in hydrochloric acid gas, dissolving the product in water, and evaporating (Chydenius).—*Potassio-thorinic chloride* is very soluble, almost deliquescent, but may be dehydrated by ignition in hydrochloric acid gas. It is likewise soluble in alcohol. When heated with potassium, it yields metallic thorinum. (Berzelius.)

Oxychloride.—In the preparation of the chloride, as above described, this compound passes over with the excess of chloride as a white cloud, which condenses to a white amorphous powder. It is decomposed by water, which dissolves chloride of thorinum, leaving the oxide.

THORINUM, DETECTION AND ESTIMATION OF. Before the blowpipe, thorinum is distinguished rather by negative than by positive characters, its oxide being unalterable, infusible, and dissolving with great difficulty in borax; the strongly saturated bead becomes milk-white on cooling; it does not form a coloured glass, either with borax or with microcosmic salt.

Thorinum is precipitated from its neutral solutions by *sulphide of ammonium*, by *ammonia*, and by *potash*, as a white hydrate, insoluble in potash.—The *fixed alkaline carbonates*, and *carbonate of ammonium*, precipitate carbonate of thorinum, soluble in excess of the precipitant; *ammonia* forms no precipitate in this solution, as it does in the corresponding solution of zirconia.—A solution of thorinum-chloride is precipitated by *ferrocyanide of potassium*, which does not form any precipitate with chloride of zirconium.—*Sulphate of potassium* produces. with thorinum-salts, a crystalline precipitate of potassio-thorinic sulphate, soluble in boiling water, but insoluble in excess of the potassium-sulphate,—a character which serves to distinguish thorinum from yttrium. From cerium and the allied metals, thorinum is distinguished by the reaction of its solutions with *hyposulphite of sodium*. which precipitates thorina, but not the oxides of the cerium-metals; from cerium and didymium also by not giving any coloured reactions before the blowpipe.—From titanium, tantalum, and niobium. it is also distinguished by its behaviour before the blowpipe, and in solution by its reaction with *oxalic acid*, which forms a white precipitate of thorinum-oxalate.

Thorinum is estimated as oxide. It is precipitated by *ammonia* as a hydrate, which on ignition yields the pure oxide.

The methods of separating thorinum from other metals are indicated in the preceding paragraph. Precipitation with *sulphate of potassium* in excess serves to separate it from all the metals contained in the sulphide of ammonium precipitate, except zirconium and the cerium-metals.—From zirconia it may be separated by treating the mixed solution with *oxalic acid*, which precipitates both the metals as oxalates; but on adding a slight excess of oxalic acid, the oxalate of zirconium dissolves completely, leaving the oxalate of thorinum behind (H. Rose, *Traité de Chimie Analytique*, ii. 101).—From the cerium-metals thorinum may be separated, as already observed, by means of *sodic hyposulphite*, which precipitates the thorinum as hyposulphite (Chydenius). The precipitation, however, is not complete, and, according to Hermann (J. pr. Chem. xciii. 106), every 1,000 pts. of water retain in solution 0·85 pt. of thorina, or in presence of salts rather less. To effect the separation. Hermann converts all the bases into neutral sulphates, dissolves 10 pts. of these mixed sulphates in 1,000 pts. of water, and heats the solution to the boiling-point with 4 pts. of sodic hyposulphite. A precipitate of thorinic hyposulphite is then formed, while the whole of the cerium-metals remain in solution. The precipitate, when ignited, leaves pure thorina, which must be weighed, and its weight corrected for the amount remaining in solution, amounting to, as above stated. 0·85 pt. The cerium must be previously brought to the state of cerous salt, if not already in that state.

From titanium, tantalum, and niobium, thorinum is most easily separated by precipitation with *oxalate of ammonium*.

Atomic Weight of Thorinum.—The atomic weight of this metal has been determined by the analysis of the sulphate, $Th''SO^4$ or $ThO.SO^3$. Berzelius, in two experiments, obtained the numbers 119·32 and 117·75, and from the mean of fifteen analyses of potassio-thorinic sulphate, $Th''K^2(SO^4)^2$, not agreeing very closely, the number 118·2. Chydenius, partly from his own (not very accordant) experiments, and partly from those of Berzelius, calculates the number 118·32. Delafontaine (N. Arch. ph. nat. xviii. 343; Jahresb. 1863, p. 198) found, as a mean of a considerable number of closely-agreeing analyses, that the sulphate crystallised from hot solutions, $4ThSO^4.9H^2O$, contains 52·51 per cent. ThO, 31·92 SO^3, and 15·80 H^2O; and that the salt crystallised at ordinary temperatures, $2ThSO^4.9H^2O$, contains 45·06 per cent. ThO, and 28·68 H^2O: hence the atomic weight of thorinum is found to be 115·72, the number now adopted.

THORINUM, FLUORIDE OF. ThF^2.—Berzelius, by treating hydrate of thorinum with hydrofluoric acid, and evaporating off the excess of acid, obtained the fluoride as an enamel-white, heavy, insoluble powder, not decomposed by ignition, and only imperfectly when heated with potassium.—The *hydrated fluoride*, $ThF^2.2H^2O$, is obtained, by double decomposition, as a white gelatinous precipitate, which is insoluble in water and in hydrofluoric acid, gives off only part of its water at 200°, and is converted by ignition into thorina. (Chydenius.)

Potassio-thorinic Fluorides.—α. The compound $KF.ThF^2.2H^2O$, is produced by boiling recently precipitated hydrate of thorinum with hydropotassic fluoride and free hydrofluoric acid, and separates as a fine heavy powder.—β. The compound $2KF.4ThF^2.H^2O$ is precipitated by hydropotassic fluoride, from a solution of thorina in hydrochloric acid. (Chydenius.)

THORINUM, IODIDE OF. Crystallises with difficulty; turns brown on exposure to light. (Chydenius.)

THORINUM, OXIDE OF, or **THORINA.** ThO.—This, the only known oxide of thorinum, is prepared from thorite or orangite, or from euxenite.—α. Thorite or orangite, in fine powder, is decomposed with hydrochloric acid; the silica is separated in the usual way, by evaporating to dryness, and digesting the residue with acidulated water; the filtered solution is treated with sulphydric acid to separate lead and tin; and the thorina is precipitated by ammonia, together with small quantities of the oxides of iron, manganese, and uranium. The precipitate is redissolved in hydrochloric acid; the nearly neutral solution is mixed with a hot saturated solution of neutral potassic sulphate, whereby the thorinum is precipitated as potassio-thorinic sulphate; and from the solution of this salt in hot water, the thorinum is precipitated by ammonia as a hydrate, which on ignition yields anhydrous thorina. Or the thorinum may be precipitated from the nearly neutral hydrochloric solution by oxalic acid, and the oxalate converted into thorina by calcination.

β. Euxenite, from Arendal,[*] which contains about 6 per cent. thorina, is calcined and finely pulverised, then heated with excess of strong sulphuric acid; the resulting pasty mass is digested with cold water, in which it is almost wholly soluble; and the solution is boiled, whereupon it deposits titanic and niobic acids; but to ensure complete separation of these acids, the ebullition must be continued for several days. The cooled and filtered liquid is then treated with ammonia to precipitate the bases, the precipitate is dissolved in hydrochloric acid, and the liquid is mixed with a hot saturated solution of potassic sulphate in excess, which precipitates the thorinum, leaving the yttrium, &c. in solution. The thorino-potassic sulphate may then be dissolved in hot water, and the thorina precipitated by ammonia. (Chydenius.)

Properties.—Anhydrous thorina is white, and has the high specific gravity 9·402 (Berzelius). According to Chydenius, the oxide obtained by ignition of the hydrate is greyish-yellow. By fusion with borax, in a porcelain furnace, it is obtained in quadratic crystals, probably isomorphous with tinstone and rutile, and having a density of 9·077 to 9·20 (Nordenskjöld and Chydenius, Pogg. Ann. cx. 642; Jahresb. 1860, p. 134). The ignited oxide is insoluble in hydrochloric and nitric acids, and dissolves in strong sulphuric acid only after prolonged heating to the boiling-point of the acid. It is not rendered soluble in nitric or hydrochloric acid by ignition with alkalis or alkaline carbonates.

Hydrate of thorinum is precipitated from solutions of thorinum-salts by caustic alkalis, as a gelatinous mass, which soon sinks to the bottom of the liquid. When left to dry in the air, it absorbs carbonic acid, and cakes into hard vitreous lumps; under the air-pump it dries up to a white powder (Berzelius). It dissolves readily in all acids, excepting oxalic, molybdic, and hydrofluoric acids. (Chydenius.)

THORINUM, OXYCHLORIDE OF. See p. 786.

THORINUM, OXYGEN-SALTS OF. These salts are colourless, and have a strongly astringent taste; those which contain volatile acids give up their acid on ignition. The behaviour of the solutions with reagents has been already described (p. 786).

Acetate of Thorinum, $Th''(C^2H^3O^2)^2$ (at 100°), forms groups of fine needle-shaped crystals, insoluble in water, and only slightly soluble in dilute acetic acid.—The *carbonate,* $Th''CO^3.3Th''H^2O^2.H^2O$, is obtained by treating the hydrate suspended in water with carbonic acid, or by precipitating a solution of the chloride with an alkaline carbonate, as an amorphous precipitate, which aggregates together in drying.—The *chromate,* $Th''CrO^4.4H^2O$, crystallises indistinctly on evaporating a solution of thorina in chromic acid. A solution of thorinum-chloride gives, with acid potassic chromate, on addition of ammonia, a yellow precipitate of a basic salt.—The *citrate* and *tartrate* are gelatinous precipitates, obtained by adding citric or tartaric acid to a neutral thorinum-salt.—The *formate,* $Th''(CHO^2)^2.2H^2O$, forms tabular efflorescent crystals, which give off 9·77 per cent. water in drying.—The *molybdate* is a white flocculent precipitate, soluble in hydrochloric acid (Chydenius).—The *nitrate*, *oxalate*, *phosphate*, and *sulphate* are described under their respective acids.

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[*] This mineral contains (according to Chydenius) 54·28 per cent. niobic and titanic oxides, 34·58 yttria and erbia, 6·28 thorina, with small quantities of ferrous and uranous oxides, and 2·60 matter volatilised by ignition (= 97·74).

THORINUM, OXYSULPHIDE OF. See below.

THORINUM, PHOSPHIDE OF. When thorinum is heated in phosphorus-vapour, the two unite with incandescence, forming a grey metallically lustrous mass, which is not attacked by water, and burns to phosphate when heated. (Berzelius.)

THORINUM, SULPHIDE OF. ThS.—Thorinum, heated with sulphur, burns in the vapour with the same splendour as in the air, forming a yellow pulverulent sulphide, which acquires metallic lustre by pressure, and is but slightly attacked by acids; nitromuriatic acid, however, oxidises it to sulphate (Berzelius). Chydenius, by igniting thorina in a mixture of hydrogen-gas and vapour of carbonic disulphide, obtained sulphide of thorinum as a black mass of specific gravity 8·29, becoming grey and metallically lustrous by trituration. It is converted by roasting into thorina, is not attacked by hydrochloric, and only slowly by nitric acid, but dissolves completely in nitromuriatic acid. By fusion with potassium-hydrate it is converted into thorina, and by heating in chlorine-gas into chloride of thorinum; it is not altered by ignition in hydrogen.

When thorina is heated only to low redness in the mixture of hydrogen and carbonic disulphide, an oxysulphide is formed, probably ThS.2ThO. (Chydenius.)

THORITE. *Orangite.*—A hydrated silicate of thorinum, occurring on the island of Lövön, not far from Brevig in Norway. It is massive and compact, of black colour, with vitreous lustre, opaque to translucent on the edges; streak greyish-red. Brittle. Hardness = 4·5 to 5. Specific gravity = 4·63. Before the blowpipe it becomes brown-red, does not melt when heated by itself, but forms, with borax, a glass coloured by iron, and on addition of soda, exhibits the manganese reaction. In its natural state, it dissolves in hydrochloric acid, with evolution of chlorine and separation of gelatinous silica, but after ignition it is scarcely attacked by hydrochloric acid.

The variety called *orangite*, found in the zircon-syenite near Brevig, is yellowish or yellow to brown, yields an orange-yellow powder, is translucent or transparent in thin splinters, has a specific gravity = 5·2 to 5·4, and hardness = 4·5.

Analyses: —*a*. Thorite (Berzelius, Pogg. Ann. xvi. 385).—*b*. Thorite, black, almost glassy: specific gravity = 4·686 (Bergemann, *ibid*. lxxiii. 561; lxxxv. 558).—*c*, *d*, *e*. Orangite: *c* by Bergemann, *d* by Damour (*ibid*. lxxxv. 555), *e* by Berlin (*ibid*. lxxxv. 556):

	SiO^2.	ThO.	U^2O^3.	Fe^2O^3.	Mn^2O^3.	CuO.	MgO	K^2O.	Na^2O.	PbO.	SnO^2.	Al^2O^3.	H^2O.		
a.	19·31	58·91	1·64	3·46	2·43	2·62	0·36	0·15	0·11	0·82	0·01	0·06	9·66	=	99·54
b.	19·21	57·00	..	..	..	..	..	..	..	..	..	..	9·17	=	
c.	17·69	71·25	..	0·31	0·21	4·04	..	0·30		..	..	..	6·90	=	100·70
d.	17·52	71·65	1·13	0·31	0·28	1·59	..	0·14	0·33	0·88	..	0·17	6·14	=	100·14
e.	17·78	73·29	0·96 *		..	0·92	..	..	..	..	..	..	7·12	=	100·07

The analysis of thorite by Berzelius leads to the formula $Th^2SiO^4.2H^2O$; those of orangite to the formula $3Th^2SiO^4.4H^2O$; but the difference of composition is most probably only apparent, and due to impurity in the thorite; indeed, orangite frequently occurs so intimately intergrown with thorite as to show that the two minerals are essentially identical, the orangite being merely the purer variety.

THORIUM. Syn. with THORINUM.

THRAULITE. A variety of hisingerite from Bodenmais in Bavaria (iii. 102).

THRIDACIUM. (from θρίδαξ, lettuce).—The inspissated milky juice of the common lettuce, *Lactuca sativa* (that obtained from *L. virosa* is called lactucarium (iii. 464). It is a grey-brown or yellow bitter substance, having an odour like that of opium, and forming with water a solution which has a brown-yellow colour and acid reaction. Tannin forms in it a copious precipitate; ammonia throws down phosphate of calcium; nitrate of barium, nitrate of silver, oxalate of ammonia, and alcohol produce turbidity. It is said to produce a sedative action, but the nature of the active principle is not exactly known. (Handw. d. Chem. viii. 821).

THROMBOLITE. A cupric phosphate occurring at Retzbanya in Hungary.

THSING-HOA-LIAO. The Chinese name for a cobaltiferous aluminic silicate used in the manufacture of porcelain; also applied to a cobaltiferous manganese-ore, used for producing a blue colour on porcelain.

THUJA. The branches of *Thuja occidentalis*, the North-American *Arbor vitæ*, contain an essential oil, wax, resin, several acids (probably including citric acid), a bitter principle, sugar, and two peculiar yellow colouring-matters, called thujin and thujigenin.

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* With traces of stannic and vanadic oxides.

When the green branches of *Thuja occidentalis* are boiled with strong alcohol, the decoction on cooling deposits a waxy substance in yellow flocks, becoming white when purified. This body, whose percentage composition is represented by the formula $C^8H^{16}O$, is a mixture of a more soluble and a less soluble substance; when saponified by lime, it yields several acids not yet examined.

When the alcoholic extract of the branches, which likewise contains volatile oil, is distilled, there remains a green resinous mass, said to contain kinovous acid, the acid likewise occurring in the needles of the Scotch fir (iv. 650). The watery liquid separated from the resin yields, on addition of neutral lead-acetate, a yellow precipitate containing thujin, together with pinitannic acid (iv. 651). The liquid filtered from this precipitate gives, with basic lead-acetate, a precipitate probably containing a little citric acid, together with an amorphous tannin, and thujigenin. The filtrate from this last precipitate contains sugar, and a bitter principle, said to be identical with the pinipicrin of the Scotch fir (iv. 651).

If the branches, after treatment with boiling alcohol, are exhausted with water containing a small quantity of alkali, the resulting solution deposits, on addition of an acid, a gelatinous substance having the composition $C^8H^{12}O^{12}$.

The leaves of thuja are said to possess medicinal properties. *Tinctura Thujæ* has been recommended as a remedy for rheumatism, gout, intermittent fever, &c.

The essential oil of thuja, which passes over on distilling the ends of the branches and the leaves with water, is, according to Schweizer (Ann. Ch. Pharm. li. 398), a mixture of several oils, and contains 77 per cent. carbon, 10·9 hydrogen, and 11·4 oxygen. It is colourless when fresh, but soon turns yellow in contact with the air; it has the odour of thuja, is lighter than water, and only slightly soluble therein, but dissolves easily in alcohol and in ether. On fractional distillation, the greater part passes over between 190° and 197°, the boiling-point quickly rising to 206°, and ultimately a brown residue is left.

Crude oil of thuja dissolves large quantities of iodine; and on heating the solution, a violent action takes place, hydriodic acid and a very volatile oil being given off. The residue, when further heated, gives off a dark viscid oil, then vapour of iodine, and leaves a residue of charcoal.

When the volatile oil just mentioned is repeatedly distilled over iodine, then over quicklime and potassium in succession, it becomes colourless, free from oxygen, like turpentine-oil in taste and odour, lighter than water, and boils between 165° and 175°. Thus purified, it constitutes Schweizer's thujene or thujone. The viscid oil, agitated with potash-ley, yields to that liquid, carvacrol (i. 808), separable by sulphuric acid. The portion insoluble in potash appears to be colophene (i. 1086).

Oil of thuja is not sensibly altered by distillation with *phosphoric acid*.—By *oil of vitriol* it is immediately resinised.—Commercial *nitric acid* turns it dark-yellow, without setting it on fire; with *potassium* it resinises without giving off hydrogen.—*Hydrate of potassium* blackens thuja-oil immediately, and resinises a portion of it, whilst another portion passes over unaltered. Repeated distillation of the portion which has gone over with hydrate of potassium diminishes its quantity, but does not perceptibly alter its external characters; after five distillations, the distillate contains 78·87 per cent. C, 10·98 H, and 10·15 O. From the black residue, water separates a resin-soap, soluble in pure water, while carvacrol remains in the alkaline solution. (Schweizer.)

THUJENE. Syn. with THUJONE.

THUJETIC ACID. $C^{28}H^{22}O^{13}$. (Rochleder and Kawalier, Wien. Akad. Ber. xxix. 14.)—This acid, which contains the elements of 3 at. water less than thujetin (*infra*), is prepared: 1. By boiling thujetin with baryta-water, adding sulphuric acid after a while, then alcohol, and filtering the liquid while hot; it then separates in microscopic crystals.—2. Together with crystallisable sugar, by boiling thujin for some hours with baryta-water in an atmosphere of hydrogen, till a reddish-yellow precipitate is formed. On passing carbonic anhydride through the liquid, filtering, and treating the washed precipitate with acetic acid to dissolve the baryta, thujetic acid remains undissolved. It forms lemon-yellow microscopic needles, soluble in alcohol, and precipitated by water.

THUJETIN. $C^{28}H^{28}O^{16}$. (Rochleder and Kawalier, Wien. Akad. Ber. xxix. 12.)—A compound obtained, together with crystallisable sugar, by heating thujin with dilute acids; the liquid, which is green at first, becomes yellow after some time, then colourless, and deposits thujetin after evaporation of the alcohol. Thujetin is likewise obtained in the preparation of thujin and thujigenin, in the manner presently to be described.

Thujetin is nearly insoluble in *water*, but dissolves in *alcohol* and in *ether*. It is not altered by dilute *hydrochloric* or *sulphuric acid*. Its alcoholic solution assumes a splendid blue-green colour on addition of *ammonia*; green with *potash*, becoming yellow, and finally red-brown on standing, and then yielding red flocks with acids. It forms red precipitates with the *neutral* and *basic* acetates of lead, colours *ferric chloride* like ink, and after a while throws down a dark-coloured precipitate. It colours *stannic chloride* dark-yellow, *nitrate of silver* blackish-grey, and *platinic chloride* gradually yellowish-brown.

By boiling with *baryta-water*, it is converted into thujetic acid: $C^{28}H^{28}O^{16} - 3H^2O = C^{28}H^{22}O^{13}$.

THUJIGENIN. $C^{28}H^{24}O^{14}$. (Rochleder and Kawalier, Wien. Akad. Ber. xxix. 10).—A compound occurring in very small quantity in *Frondes Thujæ*, the green parts of *Thuja occidentalis*, and produced, together with sugar, when thujin is heated with hydrochloric acid (p. 791).

Preparation.—Comminuted *Frondes Thujæ* are boiled with alcohol; the decoction is strained and left to cool; the deposited wax is separated; the alcohol is distilled from the filtrate; and the residue is mixed with water, a few drops of solution of neutral acetate of lead being added to facilitate the filtration. The filtrate is completely precipitated by neutral acetate of lead, and the yellow precipitate (*a*), containing thujin and thujetin, is used for the preparation of these substances. The filtered liquid, mixed with basic acetate of lead, yields a second precipitate (*b*) containing thujigenin.

a. Preparation of Thujin.—The precipitate *a* is washed with water, and dissolved in dilute acetic acid; the liquid is filtered from undissolved matter; the filtrate precipitated with basic acetate of lead; the washed precipitate decomposed under water by sulphydric acid; the liquid heated with the sulphide of lead, and filtered hot; the sulphide of lead washed with a small quantity of hot water; and the filtrate, after being freed from sulphydric acid by heating it in a stream of carbonic anhydride, is evaporated in a vacuum over oil of vitriol. The liquid, after standing for some days, deposits crystals of thujin, which are collected, dissolved in boiling water, with addition of alcohol, again left to crystallise, and recrystallised till the solution of the substance in weak spirit no longer turns green on addition of ammonia. The sulphide of lead still retains a small portion of thujin, which may be obtained by boiling with alcohol.

b. Preparation of Thujigenin.—The precipitate *b*, formed by basic acetate of lead, is washed, suspended in water, and decomposed by sulphydric acid: and the liquid is heated with the sulphide of lead, and filtered hot through a warmed filter. The filtrate, heated as above in a stream of carbonic anhydride, and evaporated in a vacuum, deposits flocks of thujigenin.

c. If the chief object is to obtain thujigenin, the liquids obtained by decomposing with sulphydric acid the two precipitates (*a* and *b*) produced by neutral and basic acetate of lead, are evaporated till thujin and thujetin separate out from them: these substances are removed, and the filtrate is mixed with hydrochloric acid, warmed in the water-bath till it begins to show turbidity, and then quickly cooled. It then deposits thujigenin, which must be collected, dissolved in alcohol, and precipitated by water.

By further heating the liquid from which the thujigenin has separated, and then cooling it, thujetin is obtained, contaminated with a red substance, from which it may be freed by repeated solution in alcohol and precipitation with water.

Properties and Reactions.—Thujigenin forms microscopic needles very slightly soluble in water, but soluble in alcohol, and precipitated almost completely by water. When boiled with *chloride of acetyl*, it turns red, and after prolonged action, is converted into acetyl-thujigenin, $C^{28}H^{22}(C^2H^3O)^2O^{14}$, a resinous body precipitable by water.

The investigation of thujigenin is still incomplete; it remains to be determined whether this substance can be formed artificially, and how far it differs from thujetin.

THUJIN. $C^{20}H^{22}O^{12}$. (Rochleder and Kawalier, *loc. cit.*)—A crystallisable glucoside, occurring in the green parts of *Thuja occidentalis*. The mode of preparing it has just been described. 240 lbs. of *Frondes Thujæ* yield only a few grammes of thujin.

Thujin forms shining lemon-yellow crystals, appearing under the microscope as four-sided tables. It has an astringent taste, and is soluble in alcohol.

The alcoholic solution is coloured yellow by *ammonia* or *potash*, red-brown with access of air, and yields a fine yellow precipitate with *neutral* or *basic acetate of lead*. It is coloured dark-green by *ferric chloride*, does not precipitate *cupric sulphate*, *platinic chloride*, or *nitrate of silver*, but the silver-solution becomes blackish-grey on addition of ammonia.

positions.—1. Thujin heated on platinum-foil burns, and leaves a carbonaceous residue, which burns away slowly, but completely.—2. When heated in alcoholic solution with dilute *hydrochloric* or *sulphuric acid*, it turns green, then yellow, and is resolved into thujetin, which separates out, and sugar. 100 pts. thujin take up 7·3 pts. water, and yield 40·48 pts. sugar and 66·78 pts. thujetin:

$$2C^{20}H^{22}O^{12} + 4H^2O = 2C^6H^{12}O^6 + C^{28}H^{28}O^{16}.$$

Thujigenin appears also to be formed when thujin is heated for a short time with hydrochloric acid (p. 790).—3. Thujin dissolves in *baryta-water*, forming a yellow solution, which, when heated, deposits an orange-yellow precipitate of thujetic acid, becoming dark reddish-yellow by continued boiling, while sugar remains in solution:

$$2C^{20}H^{22}O^{12} + H^2O = C^{28}H^{22}O^{13} + 2C^6H^{12}O^6.$$

THUJONE. A volatile hydrocarbon, obtained by the action of iodine on oil of thuja (p. 789).

THULITE. See EPIDOTE (ii. 490).

THUMITE. Syn. with AXINITE (i. 477).

THURINGITE. *Owenite.*—A silicate of iron and aluminium, occurring as an aggregate of minute scales, which are distinctly cleavable in one direction, have an olive-green colour, and nacreous lustre. Hardness = 2·5. Specific gravity = 3·18 to 3·20. Before the blowpipe it melts, with moderate facility, to a black magnetic glass; gives off water when heated in a tube; and dissolves in hydrochloric acid, with separation of gelatinous silica.

Analyses.—*a.* From Reichmannsdorff, near Saalfeld, in Thuringia (Rammelsberg, *Mineralchemie*, p. 851).—*b.* The same (Smith, Sill. Am. J. [2], xviii. 372).—*c.* Schmiederberg, near Saalfeld (Genth and Keyser, *ibid.* xvi. 167; xviii. 410).—*d.* Potomac river: *Owenite* (Smith).—*e.* The same (Genth and Keyser):

	SiO^2.	Al^2O^3	Fe^2O^3.	FeO.	MgO.	Na^2O and K^2O.	H^2O.		
a.	22·35	18·39	14·86	34·34	1·25	. .	9·81	=	101·00
b.	22·05	16·40	17·66	30·78	0·89	0·14	11·44	=	99·36
c.	23·55	15·63	13·79	34·20	1·47	. .	10·57	=	99·21
d.	23·55	16·46	14·33	32·78	1·60	0·46	10·48	=	99·66
e.	23·21	15·59	13·89	34·58	2·62	0·49	10·59	=	100·97

These analyses lead to the formula $2(2FeO.SiO^2).(Al^2O^3;Fe^2O^3)^2SiO^2.4H^2O$.

THYME, OIL OF. The herb of garden thyme (*Thymus vulgaris*, L.) yields, by distillation with water, a volatile oil, which in the fresh state is colourless or yellowish, and mobile; the oil commonly occurring in commerce, however, is red-brown or brownish-red, and becomes thicker and darker by age. It has a pleasant pungent odour of thyme, and an aromatic camphorous taste. Its specific gravity is between 0·87 and 0·90. It dissolves sparingly in *water*, in about its own bulk of *alcohol* of specific gravity 0·85, and easily in *ether*. *Iodine* acts but slightly on oil of thyme; *alcoholic potash* dissolves it. It turns the plane of polarisation to the left, a column 100 millimetres long producing a deviation of $-8°$ to $-9°$.

Oil of thyme is a mixture of at least two hydrocarbons, namely thymene, $C^{10}H^{16}$, and cymene, $C^{10}H^{14}$, together with an oxygenated camphor or stearoptene, called thymol, $C^{10}H^{14}O$ (which is said to constitute about half of the crude oil), and perhaps other oxidised products of the hydrocarbons.

On submitting the crude oil to fractional distillation, the thymene passes over between 160° and 165°, and the cymene between 170° and 180°. This latter hydrocarbon may also be separated from the thymene by treating the mixture with strong sulphuric acid, washing the undissolved portion with water, and rectifying. The hydrocarbon thus obtained has the composition $C^{10}H^{14}$, and appears to be identical in every respect with cymene obtained from Roman cumin-oil.

On continuing the distillation of the thyme-oil, there passes over, between 185° and 225°, a mixture of thymene (and cymene) with about $\frac{1}{3}$ pt. of thymol, and between 225° and 335°, pure thymol, which may be separated from the remaining portions of hydrocarbon by solution in potash-ley. (Lallemand, Ann. Ch. Pharm. ci. 119; cii. 119.)

A pound of thyme yields, according to different statements, from 20 to 90 grains of oil, the quantity, doubtless, varying with the locality in which the plant is grown.

Wild thyme (*Thymus serpyllum*) yields, by distillation with water, from 0·08 to 0·09 per cent. of a yellow oil, having an agreeable odour of lemons and thyme, and an aromatic bitter taste. Alcohol of specific gravity 0·85 dissolves it in all proportions. (Herberger, Repert. Pharm. xxxiv. 41; Zeller, *Studien über ätherische Oele*, Landau, 1850.)

THYMEID. See under THYMOÏL (p. 793).

THYMENE. $C^{10}H^{16}$. (Lallemand, Ann. Ch. Phys. [3], xlix. 155.)—A hydrocarbon belonging to the camphene-group, and constituting the most volatile portion of the oil of garden thyme, distilling between 160° and 185° (p. 791). It may be purified by agitation with potash-ley, and repeated fractional distillation over potassium-hydrate; after this treatment, however, it usually still retains a small quantity of cymene, which may be removed by fractional distillation.

Thymene is a colourless oil, having an agreeable odour of thyme, boiling at 160°—165°, and of specific gravity 0·868 at 20°. It deflects the plane of polarisation to the left, but less strongly after repeated rectification over caustic potash (Lallemand). It dissolves in *oil of vitriol*, with rise of temperature, and yields by distillation the same products as oil of turpentine.—It absorbs *hydrochloric acid gas*, with slight rise of temperature, and forms a compound which remains liquid at −20°, and, after purification with chalk and animal charcoal, contains 20 per cent. chlorine. (Lallemand.)

From the volatile oil of the seeds of *Ptychotis Ajowan*, Stenhouse obtained, by fractional distillation, dehydration with chloride of calcium of the portion which passed over below 176°, distillation over caustic potash, treatment with sodium, and rectification, a colourless, strongly refracting oil, having a pungent aromatic odour, different from that of oil of thyme, of specific gravity 0·854 at 12°, and boiling at 172°. It formed with hydrochloric acid gas a brown thin liquid. It contains 88·24 per cent. C and 11·5 H, and is therefore $C^{10}H^{16}$, and perhaps identical with Lallemand's thymene. According to Haines (Ann. Ch. Pharm. xcviii. 315), it consists of cymene, $C^{10}H^{14}$.

THYMICIC ACID. Syn. with THYMOTIC ACID (p. 795).

THYMINE. This name was applied by Gorup-Besanez to a crystallisable, slightly basic substance, obtained from the thymus-gland, which, however, he afterwards found to be identical with leucine.

THYMOÏL. $C^{12}H^{16}O^2$. (Lallemand, Ann. Ch. Phys. xlix. 160; Ann. Ch. Pharm. cii. 119.)—A product of the oxidation of thymol. It is obtained by dissolving thymol in excess of sulphuric acid, diluting the liquid with five or six times its volume of water, and gradually mixing it in a retort with manganic peroxide or potassic dichromate; great heat is then evolved, and on distilling the liquid, water passes over, together with formic acid, and a yellow oil which soon solidifies. This substance, which is thymoïl, may be purified by recrystallisation from ether-alcohol.

Thymoïl forms reddish-yellow, four-sided, shining, crystalline laminæ, having an aromatic odour, recalling at the same time that of iodine and that of chamomile. It is heavier than *water*, only slightly soluble therein, sparingly soluble also in *alcohol*, easily in *ether*. It melts at 48°, gives off copious vapours at 100°, sublimes at a stronger heat, and boils with partial decomposition at about 235°, leaving in the retort a dark-red oily residue, which solidifies on cooling to a violet metallically lustrous mass.

Thymoïl is easily altered by light; when exposed to sunshine for some days in a sealed tube, it becomes quite black, and is converted into a mixture of several compounds, from which alcohol extracts thymoïlol and thymeid, together with other substances, and leaves a small quantity of a yellowish powder, consisting of oxythymoïl, $C^{12}H^{16}O^3$. This body is insoluble in water and in alcohol, sparingly soluble in ether, melts without decomposition at 100°, is insoluble in alkalis, and is, on the whole, a very indifferent substance.

Thymoïl dissolves in strong sulphuric or nitric acid at ordinary temperatures, and is separated therefrom unaltered by water. If the action of the acids be long continued, or assisted by heat, decomposition takes place, but the products have not been examined.

Chlorine acts slowly on thymoïl, and only when assisted by heat, forming chlorinated substitution-products.

Fused thymoïl slowly absorbs dry *ammonia-gas*, forming thymoïlamide, $N.H^2.C^{12}H^{15}O$, a dark-red, uncrystallisable, hard, brittle mass, which softens at 100°, so that it may be drawn into threads, and is soluble in alcohol.

In contact with *potash-ley*, thymoïl quickly absorbs oxygen from the air, and dissolves to a brown-red liquid, containing the potassium-salt of thymoïlic acid:

$$\underset{\text{Thymoïl.}}{4C^{12}H^{16}O^2} + O^{12} = \underset{\substack{\text{Thymoïlic}\\\text{acid.}}}{C^{48}H^{62}O^{19}} + H^2O;$$

The thymoïlate of potassium may be obtained by saturating the liquid with carbonic acid, evaporating to dryness, and exhausting the residue with alcohol; and on decomposing the solution of this salt with hydrochloric acid, thymoïlic acid is obtained, in yellow uncrystallisable flocks, sparingly soluble in water. All the thymoïlates, except the silver- and lead-salts, are soluble in water. The lead-salt has the composition $C^{48}H^{62}\overset{\prime\prime}{Pb}{}^{3}O^{13}$, showing that the acid is tribasic.

Thymoïl, under the influence of *reducing agents* (such as nascent hydrogen, sulphurous acid, ferrous sulphate, and stannous chloride), takes up 2 at. hydrogen, and is converted into thymoïlol, $C^{12}H^{18}O^2$, a compound homologous with colourless hydroquinone (iii. 213).

Strong aqueous sulphurous acid colours thymoïl dark-violet at first, but this colour disappears again, and after a few days the thymoïl is found to be converted into white flocculent thymoïlol, which may also be obtained, in a similar manner, by treating thymoïl with stannous chloride, &c. By recrystallisation from alcohol, it is obtained in small, colourless, four-sided prisms, which are inodorous and tasteless, dissolve sparingly in water, easily in alcohol and ether, melt at 145°, and distils without decomposition at 290°.

By the action of *oxidising agents*, thymoïlol is reconverted into thymoïl, this transformation being produced almost instantly by nitric acid, chlorine-water, ferric chloride, silver-nitrate, or potassic dichromate. In the oxidation of thymoïlol, however, as well as in the action of reducing agents upon thymoïl, a transient violet coloration is produced, indicating the formation of a body intermediate between thymoïl and thymoïlol. This body, thymeïd, $C^{24}H^{34}O^4 = C^{12}H^{16}O^2$ (thymoïl) + $C^{12}H^{18}O^2$ (thymoïlol), is obtained pure by mixing equal weights of thymoïl and thymoïlol in alcoholic or ethereal solution. The liquid then immediately assumes a blood-red colour, and yields, on evaporation, violet crystals, which exhibit by reflected light a greenish metallic lustre, like that of the wing-cases of many insects.

From these relations, thymoïl may be regarded as homologous with quinone, thymoïlol with colourless hydroquinone, and thymeïd with green hydroquinone or quinhydrone; thus,—

$$\underset{\text{Thymoïl.}}{C^{12}H^{16}O^2} + \underset{\text{Thymoïlol.}}{C^{12}H^{18}O^2} = \underset{\text{Thymeïd.}}{C^{24}H^{34}O^4}.$$

$$\underset{\text{Quinone.}}{C^{6}H^{4}O^2} + \underset{\text{Hydroquinone.}}{C^{6}H^{6}O^2} = \underset{\text{Quinhydrone.}}{C^{12}H^{10}O^4}.$$

THYMOÏLAMIDE.
THYMOÏLIC ACID. } See under THYMOÏL.
THYMOÏLOL.

THYMOL. $C^{10}H^{14}O = \left.\begin{matrix}C^{10}H^{13}\\ H\end{matrix}\right\}O$. *Thymylic Hydrate. Thymylic Alcohol. Thymylic Acid. Camphor* or *Stearoptene of Thyme-oil.*—This compound, the oxygenated constituent of thyme-oil (p. 791), is isomeric with cymylic alcohol (ii. 298), and homologous with phenol. It was first obtained from thyme-oil by Doveri (Ann. Ch. Pharm. lxiv. 374), and afterwards examined more particularly by Lallemand (Ann. Ch. Phys. [3], xlix. 148; Ann. Ch. Pharm. cii. 119); it appears to be identical with the stearoptene of the volatile oil of horsemint (*Monarda punctata*, L.), which was examined by Arppe (Ann. Ch. Pharm. lviii. 42), and with that of the oil of *Ptychotis Ajowan*, an East Indian umbelliferous plant, examined by Stenhouse and by Haines (iv. 746).

Preparation.—Thymol is obtained from thyme-oil, of which it forms about one-half, by fractional distillation, passing over chiefly between 225° and 235°. The more volatile portion, however (chiefly consisting of thymene and cymene, p. 791), likewise contains considerable quantities of thymol, which may be obtained by agitating the liquid with soda-ley, separating the undissolved oil, diluting the alkaline solution with water, and supersaturating it with hydrochloric acid. Part of the thymol sometimes crystallises spontaneously from the thyme-oil on cooling. Thymol is purified by crystallisation from alcohol.

Thymol is likewise obtained from the volatile oil of horsemint, and from that of *Ptychotis Ajowan* by fractional distillation and recrystallisation.

Properties.—Thymol crystallises in transparent rhomboïdal plates, with angles of 97° 30′, striated parallel to the lateral faces, and often aggregated into irregular six-sided tables (Arppe). From the oil of *Ptychotis Ajowan*, it crystallises (according to W. H. Miller) in rhombohedral crystals; from alcoholic solution in very thin plates, which appear monoclinic in consequence of the great development of two parallel rhombohedral faces. (For the angular measurements, see *Gmelin's Handbook*, xiv. 410.)

Thymol has a mild odour, which (according to Lallemand) is quite distinct from that of thyme-oil, and an aromatic peppery taste. In the solid state, it is somewhat heavier than water; specific gravity = 1·0285; in the liquid state rather lighter. It does not act on polarised light. Its melting-point is variously stated. According to Lallemand, it melts at 44° to a colourless liquid, and remains fluid for a long time after cooling; but if pure, it solidifies immediately when touched by a solid body. According to Arppe, it melts at 48°, and does not solidify till cooled to 27°. Thymol from the oil of *Ptychotis Ajowan* melts, according to Haines, at 53°; according to Stenhouse, at 44°. Thymol boils at 230° (Doveri; Lallemand), at 231° (Haines), at 222° (Stenhouse), and distils without decomposition. Vapour-density, obs. = 5·4; calc. = 5·2.

Thymol dissolves in about 300 pts. of *water*, easily in *alcohol*, *ether*, and *strong acetic acid*, and is not precipitated from the alcoholic solution by water. It is not altered by aqueous *ammonia*, but takes up a large quantity of *gaseous ammonia*, becoming liquid, but resolidifying after the ammonia has escaped. It dissolves in aqueous *potash* and *soda*, forming compounds which are soluble in water and in alcohol; but are very unstable, being decomposed by acids, even by the carbonic acid of the air, with separation of thymol.

When thymol-vapour is passed over *soda-lime* heated to dull redness, no gas is evolved, but a crystallisable thymolate of sodium, $C^{10}H^{13}NaO$, is formed, which melts when heated, and when dissolved in water forms precipitates with mercuric chloride and silver-nitrate. The mercury-compound, which is a basic salt, $C^{20}H^{26}Hg''O^2.Hg''O$, has a greyish-violet colour, is not decomposed at ordinary temperatures by dilute sulphuric or nitric acid, but is decomposed by hydrochloric acid, with separation of thymol. Alcoholic thymol does not precipitate the alcoholic solution of neutral lead-acetate; neither does it precipitate silver-nitrate, even after addition of ammonia.

Decompositions of Thymol.—1. Thymol is somewhat altered by repeated distillation, the liquid which passes over containing less carbon than the original substance (Stenhouse).—2. It is decomposed by *phosphoric anhydride*, but the products have not been obtained in very definite form.—3. Strong *sulphuric acid*, at 50°—60°, converts it into thymylsulphuric acid $C^{10}H^{14}SO^4$; but when heated with excess of sulphuric acid to 240°, it yields sulphodraconic acid (p. 521).—4. It dissolves in *glacial acetic acid*, and subsequent addition of sulphuric acid forms acetothymylsulphuric acid, $C^{12}H^{16}SO^5 = (C^2H^3O)(C^{10}H^{13})SO^4$ (Lallemand).—5. Thymol is easily oxidised by *chromic acid*, or by a mixture of sulphuric acid and manganic peroxide, yielding a distillate containing formic acid and thymoïl, $C^{12}H^{16}O^2$ (p. 792), and a residue consisting of a brown acid, solid and friable at ordinary temperatures, and dissolving with dark-red colour in alcohol.—6. *Nitric acid*, whether dilute or concentrated, acts violently on thymol, giving off nitrous and carbonic anhydrides, and forming a number of products, chiefly resinous bodies, and a large quantity of oxalic acid.—7. *Chlorine* in diffused daylight acts with great violence on thymol, with rise of temperature, and elimination of hydrochloric acid gas, the thymol remaining liquid, and assuming a wine-red colour at the beginning of the action. If too great heat be avoided, the product consists of trichlorothymol; then, if the passage of the chlorine be continued in bright daylight, a very viscid oil is formed, from which pentachlorothymol gradually crystallises (Lallemand).—8. *Oil of thyme*, distilled with 8 pts. chloride of lime and 24 pts. water, yields chloroform (Chautard, Compt. rend. xxxiv. 485).—9. *Bromine*, in sunshine, converts thymol into pentabromothymol (Lallemand).—10. Thymol is not altered by *hydrochloric acid* (Stenhouse). When hydrochloric acid gas is passed over thymol, it quickly assumes a brown, and, after removal of the excess of hydrochloric acid, a purple-brown colour, but does not increase in weight by more than 2 to 3 per cent., even when heated; on distilling the product, unaltered thymol is first obtained, then a red substance (Arppe).—11. Thymol gently heated with *sodium* in a stream of *carbonic anhydride*, takes up the elements of the latter, forming thymyl-carbonic acid, $C^{11}H^{14}O^3 = C^{10}H^{14}O.CO^2$, together with thymotic acid, an acid isomeric therewith. (Kolbe and Lautemann, p. 795.)

Derivatives of Thymol.

Pentabromothymol, $C^{10}H^9Br^5O$.—Thymol subjected to the action of bromine, ultimately in sunshine, is completely converted into a solid, white, earthy mass of pentabromothymol, which may be recrystallised from ether, melts at a rather high temperature, with incipient decomposition and evolution of hydrobromic acid, but apparently without simultaneous formation of hydrocarbon. (Lallemand.)

Chlorothymols.—*a. Trichlorothymol*, $C^{10}H^{11}Cl^3O$, is obtained by passing chlorine-gas into thymol in diffused daylight (taking care to avoid too much heating), till the thymol has absorbed a quantity of chlorine equal to two-thirds of its weight. On leaving the product to stand, long yellow needles are formed, which ultimately cause it to solidify: they may be purified by expressing the remaining liquid, and recrystallising from ether-alcohol.

Trichlorothymol crystallises in lemon-yellow, oblique rhombic prisms, which melt at 61°, and have an intoxicating odour. It decomposes at 180°.—Heated with *oil of vitriol* to 100°, it is converted into a colourless liquid, which floats on the oil of vitriol, solidifies on cooling, and, after solution in aqueous potash, precipitation with hydrochloric acid, and drying, forms silky talc-like flocks. This substance has at first an agreeable odour of benzoin, melts at 45°, and distils without decomposition at 250°; it dissolves in ammonia, and forms a salt crystallising in slender needles,—whence it is probably trichlorophenol, with which it appears to agree in composition.

β. *Pentachlorothymol*, $C^{10}H^{9}Cl^{5}O$. (Lallemand, *loc. cit.*)—When thymol is exposed for a considerable time to the action of dry chlorine-gas in bright daylight, a reddish-yellow glutinous oil is formed, in which, after a while, crystals of pentachlorothymol appear: they may be purified by recrystallisation from ether.

This compound forms colourless, very hard crystals, having the form of trichlorothymol (according to another statement of Lallemand, it has the form of thymol), melting at 98°. It decomposes at 200°, giving off hydrochloric acid gas and tritylene-gas, $C^{3}H^{6}$, while a solid product (trichlorotoluenol, $C^{7}H^{5}Cl^{3}O$) collects in the neck of the retort, and charcoal remains behind:

$$2C^{10}H^{9}Cl^{5}O \;=\; C^{7}H^{5}Cl^{3}O \;+\; C^{3}H^{6} \;+\; 7HCl \;+\; CO \;+\; C^{9}.$$

In one experiment, in which very pure pentachlorothymol was heated, the carbonic oxide evolved towards the end of the process was mixed with marsh-gas, and the solid distillate, melting at 150°, and crystallising from alcohol in needles, had the composition of tetrachlorotoluenol:

$$4C^{10}H^{9}Cl^{5}O \;=\; 2C^{7}H^{4}Cl^{4}O \;+\; 2C^{3}H^{6} \;+\; 12HCl \;+\; CH^{4} \;+\; 2CO \;+\; C^{17}.$$

Impure pentachlorothymol yielded also, by distillation, a large quantity of liquid product, which, after the solid products had been removed by weak potash-ley, boiled at 265° (or, according to Lallemand's first statement, at 365°), and had the composition of dichlorocumene, $C^{9}H^{10}Cl^{2}$.

Nitrothymols.—These compounds, which possess acid properties, are probably formed by the direct action of nitric acid upon thymol, but they are more easily prepared from thymylsulphuric acid. (Lallemand, Ann. Ch. Phys. [3], xlix. 152.)

α. *Dinitrothymol*, or *Dinitrothymic Acid*, $C^{10}H^{12}(NO^{2})^{2}O$.—When nitric acid is slowly dropped into thymylsulphuric acid, or into the solution of a thymylsulphate, the liquid becomes slightly warm, and deposits dinitrothymol as a reddish oil, which soon solidifies in crystals. This compound melts at 55°, is sparingly soluble in water, and dissolves in all proportions of alcohol and ether. It is converted, by a mixture of nitric and sulphuric acid, into trinitrothymol, and by alcohol and sulphuric acid, into ethylic dinitrothymolate.—With bases it forms salts, which crystallise in silky needles, detonate at 150°, and dissolve sparingly in water, to which however they impart a strong colour.—The *potassium-salt* is orange-yellow in the anhydrous, red in the hydrated state, very slightly soluble in water.—The *lead-salt*, $C^{20}H^{22}Pb''(NO^{2})$, is very sparingly soluble in water; so likewise is the *silver-salt*.

β. *Trinitrothymol*, or *Trinitrothymic Acid*, $C^{10}H^{11}(NO^{2})^{3}O$.—To prepare this compound, dinitrothymol is dissolved in sulphuric acid, and a small quantity of nitric acid is gradually added, without allowing the mixture to get hot. On diluting with water, yellowish flocks of trinitrothymol are precipitated, which may be recrystallised from boiling water. It forms beautiful yellow needles, which melt at 100°, and decompose suddenly at a higher temperature; dissolves sparingly in cold *water*, easily in *alcohol* and in *ether*.—A mixture of *oil of vitriol* and *alcohol* readily converts it into solid trinitrothymic ether.

It unites with *bases*, forming yellow or orange-yellow salts, which detonate at 150°, and dissolve in water more readily than the dinitrothymates. The aqueous solution of trinitrothymate of potassium precipitates the salts of the heavy metals.—*Trinitrothymate of lead* contains 28·83 per cent. lead-oxide, and is therefore $C^{20}H^{20}Pb''(NO^{2})^{6}O^{2}$.

THYMOTIC ACID. $C^{11}H^{14}O^{3} = C^{10}H^{14}O.CO^{2}$. (Kolbe and Lautemann, Ann. Ch. Pharm. cxv. 205.)—This acid, isomeric with thymyl-carbonic acid, $C^{10}H^{13}.H.CO^{3}$, is prepared by gently heating thymol with sodium in a flask through which a rapid current of carbonic anhydride is passed. A viscid yellowish-brown mass is thereby formed, containing thymyl-carbonate and thymotate of sodium; and by decomposing this mass with hydrochloric acid, agitating the liquid with excess of ammonium-carbonate, and boiling down the liquid separated from the thymol till it exhibits a faint acid reaction, a clear solution of sodic thymotate is obtained, from which, on addition of hydrochloric acid, thymotic acid separates in colourless flocks, containing a little resin. It is purified by distillation with water, partly going over with the water, and partly remaining as a crystalline deposit in the condensing tube.

Thymotic acid thus prepared is a white, loosely coherent, crystalline mass, having a silky lustre. It is nearly insoluble in cold, and only slightly soluble in boiling water; from the boiling saturated solution it crystallises, by slow cooling, in long slender needles; when boiled with water, it gives off pungent irritating vapours. It melts at 120°, expands in solidifying, and may be sublimed without alteration.

Thymotic acid, left in contact with a warm solution of *ferric chloride*, dissolves with fine blue colour; the neutral solution of the ammonium-salt is immediately coloured deep blue by ferric chloride.—Thymotic acid heated with *caustic baryta* is resolved into thymol and carbonic anhydride. (Kolbe and Lautemann.)

By *pentachloride of phosphorus*, it is converted into thymotide (Naquet):

$$\underset{\text{Thymotic acid.}}{C^{11}H^{14}O^{3}} + PCl^{5} = PCl^{3}O + 2HCl + \underset{\text{Thymotide.}}{C^{11}H^{12}O^{2}}.$$

The thymotates of the *alkali-metals* are soluble in water.—The *barium-salt* is obtained in large tables or laminæ, by dissolving the acid in baryta-water, and separating the excess of baryta with carbonic acid, or by mixing thymotate of ammonium with chloride of barium, and evaporating. The lead-, copper-, and silver-salts are flocculent precipitates.

THYMOTIDE. $C^{11}H^{12}O^{2}$. (Naquet, Bull. Soc. Chim. [1865], ii. 92.)—A body produced by the action of pentachloride of phosphorus on thymotic acid (*supra*), or by heating the latter to 200° with phosphoric anhydride. To prepare it, 1 at. sodic thymotate is heated with 2 at. phosphoric pentachloride (the action begins, however, in the cold), the heat being ultimately raised to 200°. Hydrochloric acid and phosphoric oxychloride are then given off, and a pasty mass remains, which, when freed from the oxychloride by water, dissolves completely in ether. The ethereal solution leaves, on evaporation, a gummy residue free from chlorine, which gives up to boiling water an acid, forming a white precipitate with ferric salts (probably thymyl-phosphoric acid); from the residue, dilute potash extracts thymotic acid. The portion then remaining undissolved consists of thymotide and a yellowish resin having nearly the same composition.

Thymotide crystallises from alcohol in white, mostly microscopic needles, which melt at 187°, are not altered by hot potash-ley or by heating to 200° with water, but by fusion with potassium-hydrate are converted, without evolution of gas, into thymotic acid.

THYMUS. See Thyme, Oil of (p. 791).

THYMUS-GLAND. (Gorup-Besanez, Ann. Ch. Pharm. lxxxix. 115; xcviii. 1.—Städeler and Frerichs, Müller's Archiv. [1854], p. 383; Wiener med. Wochenschr. [1854], No. 30; Verhandl. d. naturforsch. Gesellsch. z. Zürich, Bd. iii. u. iv.; J. pr. Chem. lxxii. 48.—Scherer, Ann. Ch. Pharm. cvii. 314.—Friedleben, *Die Physiologie der Thymusdruse*, Frankfurt, 1858.)—This gland, called "sweetbread" in the calf and lamb, is an organ situated in front of the pericardium and the large vessels arising from the base of the heart. In the embryo and the infant, it has, in proportion to the rest of the body, a very considerable size, but in after-life it becomes comparatively smaller, and at last nearly disappears. It has been found to contain, besides water and the chemical constituents of its solid tissue, the following organic compounds:—soluble albumin, leucine, sarcine, xanthine, volatile fatty acids (including formic and acetic acids), also lactic acid, succinic acid, sugar, and extractive matters. The inorganic constituents are potash, soda, magnesia, lime, phosphoric acid, sulphuric acid, chlorine, and ammoniacal salts. Gorup-Besanez found in the thymus-gland of the calf, a crystallisable, slightly basic substance, which he at first regarded as a peculiar compound, and designated as thymine, but he afterwards found that it was identical with leucine. The juice of the fresh gland mostly has a slight acid reaction, rarely alkaline or neutral.

According to Friedleben, the quantity of fat in the gland increases considerably with the age of the animal, whereas the amounts of gluten and albumin exhibit but small differences at different ages. The proportion of earthy phosphates gradually increases, with the growth of the animal, up to a certain point, and afterwards diminishes. The amount of potash exceeds that of soda. Friedleben found the quantity of potash at all periods of life to be nearly constant, varying only from 31·8 to 32·8 per cent., whereas the soda in a calf of ten days to three weeks old, amounted to only 16 per cent., while in young oxen of twelve to eighteen months it was from 23 to 24 per cent. The aqueous extract of the thymus-gland of the calf leaves an ash almost wholly soluble in water, and containing potash in large quantity, pyrophosphoric acid, and chloride of sodium, together with small quantities of magnesia and sulphuric acid. Gorup-Besanez found the proportion of potash to soda in one case to be 2·18 : 0·60; in another, 9·95 : 3·21. The quantity of phosphoric acid (anhydride ?) to that of chlorine was, in one experiment, as 23·25 : 14·34. According to Friedleben, the quantity of lime in the thymus exceeds that of magnesia; Gorup-Besanez, however, found the contrary proportion. (Handw. d. Chem. viii. 836.)

THYMYL. $C^{10}H^{13}$.—The radicle of thymol and its derivatives.

THYMYL, HYDRIDE OF. $C^{10}H^{13}.H$.—Cymene (ii. 295) may be supposed to be thus constituted.

THYMYLSULPHURIC ACID. $C^{10}H^{14}SO^4 = (C^{10}H^{13})HSO^4 = \left.\begin{matrix}(SO^2)''\\ C^{10}H^{13}\\ H\end{matrix}\right\}O^2$. *Sulphothymic Acid.* (Lallemand, Ann. Ch. Phys. [3], xlix. 150.)—Thymol dissolves abundantly in oil of vitriol at 50°—60°, and solidifies on cooling to a crystalline mass, having only a faint red colour. By dissolving this mass in water, and saturating the solution with carbonate of barium or carbonate of lead, sulphothymate of barium or lead is obtained, from which the sulphothymic acid may be separated, and crystallised by evaporating its aqueous solution in a vacuum. It crystallises in translucent pearly tables or prisms, which contain $C^{10}H^{14}SO^4.H^2O$, and do not deliquesce on exposure to the air, but are very soluble in water.

Its aqueous solution, treated with *nitric acid*, forms dinitrothymol; with sulphuric acid and *peroxide of manganese*, or *dichromate of potassium*, it forms thymoïl (p. 792).

With bases it forms the thymyl-sulphates, $C^{10}H^{13}MSO^4$, which crystallise in forms of the monoclinic system. They decompose at 120°, with violet-red colouring, and volatilisation of thymol.—The *ammonium-salt*, which separates from its aqueous solution in well-developed crystals, also the *potassium-* and *sodium-salts*, leave, when thus treated, anhydrosulphates.* The sulphothymates dissolve very easily in water and in absolute alcohol, somewhat less in ether.

Acetothymylsulphuric Acid, $C^{12}H^{6}SO^5 = \left.\begin{matrix}C^{10}H^{12}(C^2H^3O)\\ H\end{matrix}\right\}SO^4$. *Sulphacetothymic Acid.* (Lallemand, *loc. cit.*)—When thymol is dissolved in glacial acetic acid, and oil of vitriol containing a little anhydrous sulphuric acid is added to the mixture, combination takes place at a gentle heat; and the liquid, on cooling, deposits a crystalline mass, which must be dried on porous earthenware, and freed from excess of acetic acid, by leaving it over quicklime in a vacuum.

The acid is soluble in *water*. With bases it forms crystallisable salts, which become anhydrous without decomposition at 110°, but are decomposed, with liberation of acetic acid, when their aqueous solutions are boiled or quickly evaporated. The salts are soluble in water and in alcohol.

Sulphacetothymate of Barium, $C^{24}H^{30}Ba''S^2O^{10}$, is obtained by saturating the acid with carbonate of barium.

THYMYLSULPHUROUS ACID. $C^{10}H^{14}SO^3$. Syn. with CYMYLSULPHUROUS ACID (ii. 299).

TICUNAS POISON. An arrow-poison, used by the Tecunas (or Ticunas) and other Indian tribes dwelling near the Amazon. When given to animals, it produces strong convulsions, lasting for hours. It probably contains picrotoxin, like other South-American arrow-poisons; but it has not been accurately investigated.

TILE ORE. The earthy variety of native cuprous oxide (ii. 70).

TILKERODITE. Selenide of lead and cobalt (iii. 557).

TILLANDSIA. A genus of monocotyledonous plants, belonging to the natural order *Bromeliaceæ*. *T. usneoïdes* (called *Barbe de vieillard* by the French, *Barba de Pao* by the Portuguese) is a parasitical plant, growing on trees in Carolina and the West Indies, and having long, wiry, contorted stems, which creep along the trunks and branches of old trees, and sometimes hang down in a bunch, like the hairs of a horse's tail. These stems, when stripped of their leaves and bark, are used as packing material instead of horsehair. *Tillandsia recurvata*, growing in Peru, is also used for the same purpose.

According to Avequin (J. Pharm. [3], xxxv. 95), 100 pts. of the dried plant of *T. usneoïdes* [at what temperature ?] yield 3·23 per cent. ash, containing, in 100 pts., 35·4 carbonate, phosphate, sulphate, and chloride of potassium, 18·5 lime and carbonate of calcium, 28·6 phosphates of calcium and magnesium, and 17·4 silica, with traces of lime and magnesia.

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* Unless the salts contain water of crystallisation, it is not easy to understand how thymol can be formed from their decomposition, inasmuch as it contains 14 at. hydrogen, whereas the anhydrous sulphothymates contain only 13 at.: $2C^{10}H^{13}MSO^4 = (2C^{10}H^{14}O - H^2O) + M^2SO^4.SO^3$.

Tillandsia dianthoïdea (L.), an air-plant, which does not grow in immediate contact with the soil, nevertheless contains from 6 to 8 per cent. ash, consisting chiefly of silica, together with lime and magnesia, and traces of alkalis, phosphoric acid, manganese, iron, sulphuric acid, chlorine, &c. (De Luca, Compt. rend. li. 176.)

TIMA. A medicinal preparation, introduced of late years as a remedy for phthisis. It is imported from Tampico, and is said to be prepared as a syrup, by boiling the fruits of *Crescentia edulis* with sugar, and mixing the product with almond-oil. (Arch. Pharm. [3], cvii. 375; Handw. d. Chem. viii. 840.)

TIMAZITE. Breithaupt's name for a rock, occurring in Eastern Servia, formerly regarded as belonging to the trachytes. It is porphyritic, and related to diorite, or to the so-called greenstones.

TIN. *Étain. Zinn. Stannum.—Atomic weight*, 118; *Symbol*, Sn.—This metal has been known from the earliest times: it is mentioned by Moses (Numbers xxxi. 22). The Phœnicians, long before the Christian era, fetched the metal **Κασσίτερος** from the British Isles, anciently called the Cassiterides. The word **Κασσίτερος** appears, however to have been applied in very ancient times, and the Latin word *stannum* somewhat later, not so much to tin as to certain white metallic alloys; at all events, tin and lead were regarded as similar metals, and were often confounded. Even Pliny sometimes does not use the word *stannum* for tin, but designates this metal as *Plumbum album*, s. *candidum*, in contradistinction to lead, or *Plumbum nigrum*. It was not till the fourth century of the Christian era that *stannum* was applied to the metal now called tin (Kopp's *Geschichte*), which was afterwards named Jupiter by the alchemists, and represented graphically by the symbol of that planet, ♃.

Occurrence and Distribution.—Tin occurs much less frequently than many other metals, as iron, copper, lead, zinc, &c., as the commercial supplies of it are drawn from comparatively few localities, Devonshire and Cornwall yielding by far the largest quantity. The stream-works of the peninsula of Malacca and the Dutch island of Banca probably rank next in importance. The exports from Bolivia are now very considerable, and large quantities have of late years been extracted from the mines of Saxony and Bohemia. A valuable addition of the metal has been obtained from Australia, shipped almost entirely from the port of Melbourne. The Australian tin contains, at times, so large an amount of gold, that the latter can be profitably extracted. No other deposits, of sufficient magnitude to be the object of mining explorations on any considerable scale, are at present known; but oxide of tin (*Cassiterite*) has been found in small quantities in the Isle of Man, Ireland, Greenland, France, Gallicia, Spain, Silesia, in the Fichtel and Riesengebirge in Germany, in Russia, the United States, Mexico, and Brazil. No mines are worked in Peru, but the name Peruvian tin has originated from the produce of the mines of Oruro and Carabuco, in Bolivia, being exported from Arica, a seaport on the Peruvian coast.

Tin occurs in the metallic state, somewhat more frequently as disulphide, in tin-pyrites, but most abundantly as dioxide or stannic oxide, forming the ore called tinstone, or cassiterite.

Native Tin (metallic tin) has been described by Hermann as occurring in the gold-sands of Siberia, and by Forbes in the auriferous drift of Tipuani in Bolivia; but as both these specimens contain lead, a metal seldom present together with tin-ores, it may be doubted whether the tin so found may not have been derived from artificial sources. Native tin has also been reported from Oruro, in Bolivia. (Forbes, Phil. Mag. [4], xxix. 133.)

Tin-pyrites (stannine, bell-metal ore, *Zinnkies*) is found in small quantities in the tin-veins of Cornwall, Saxony, and Oruro (Bolivia). It has the composition of a cuproso-ferrous sulphostannate, $\left.\begin{matrix}Cu^2S\\Fe''S\end{matrix}\right\}SnS^2$, the iron being generally more or less replaced by zinc; it contains from 14 to 30 per cent. of tin.

Cassiterite (tinstone, stream-tin, wood-tin), the dioxide or bioxide of the metal, SnO^2, may be regarded as the only ore of tin found in sufficient quantity to be the subject of mineral exploration; it is found both in veins and in alluvial drift-deposits, accompanied in many cases by tungsten, generally as wolfram, as in Cornwall, France, Saxony, Bohemia, Bolivia, &c. In the alluvial deposits, native gold is generally, if not invariably, found to accompany cassiterite, as is the case in Cornwall, Ireland, Virginia, Bolivia, Australia, &c. Although tin seldom enters into the composition of other minerals, it seems to be characteristic, though occurring only in very minute quantities, in some of the compounds of niobic or columbic, tantalic, and thus it has been observed in columbite, pyrochlore, tyrite, tantalite, fergusonite, aeschynite, polymignite, &c. Traces of tin have been ur in meteorites, and also in a variety of iron-pyrites from Spain.

Cassiterite is found in Cornwall, in veins or small strata, which traverse primitive rocks, mixed with other metals, such as copper, zinc, arsenic, and tungsten; the veins are of varying thickness. It is sometimes also found in numerous ramifications of small veins or "Stockwerke," which occur in felspar, porphyry, or in a granite which frequently has its felspar disintegrated into *kaolin*, or china-clay. These little veins seldom exceed six inches in width, and are frequently not nearly so wide; they run generally east and west, with a dip almost vertical; this description of ore is the common "tinstone."

The lodes in Cornwall are grouped into three districts, namely: first, in the south-west of the county, beyond Truro, near Helston; secondly, in the neighbourhood of St. Austell; and thirdly, in the vicinity of Tavistock, in Devonshire.

Many of the lodes traversing granite are worked profitably, as the rock in which they occur is generally softened by decomposition. As a general rule, the veins having an easterly or westerly direction are those which have the ore in profitable abundance, while those ranging northerly and southerly often contain other metals.

Although there are numerons exceptions, yet, as a whole, the distribution of this ore is somewhat marked. Certain combinations of rocks appear to be the conditions which may have assisted in rendering the ores of one metal more abundant than those of another in the range of parts of the same mineral lode. For instance, it is often found that a lode is cupriferous amid the slate-country, and chiefly stanniferous towards the granite. Some of the copper-veins in Cornwall have been worked for tin upon their *backs*, as the upper part of mineral veins are often termed in the mining districts, and have been abandoned when copper-ore was obtained beneath. In other places, copper has been found between tin; at Dalcoath mine, Camborne, tin occurred in profitable quantities in the *depth*, after the vein had been worked chiefly for copper, the *higher* portions having formerly furnished tin as the principal ore.

If tin be discovered first, it sometimes disappears, after sinking a certain depth, and is succeeded by copper; in others, tin is found to the depth of more than 300 fathoms beneath the surface. If a copper lode meets one of tin, it usually passes through it, and heaves it out of its course.

Metallurgy of Tin.—Tin, as above stated, is entirely extracted from the dioxide, The *vein*-tin requires much care in dressing, to separate mechanically the various foreign substances which it contains. The preliminary operations are:—

1. Cleansing the rough ore as it comes from the mine. This is sometimes done by placing the ore on a grating, allowing water to fall over it from some elevation, or by agitating it with a stream of water.

2. Sorting the cleansed ore into four qualities:

I. That which is rich in tin.
II. That containing tin and other metals.
III. That containing copper-ore.
IV. Stony gangue, or useless ingredients.

3. Stampingor rolling the ores No. I. into a certain fineness, according to its quality, which is of so much importance that it is regulated by a copper plate pierced with a certain number of holes in the square inch, placed in front of the stamp-box, through which everything from the stamping-mill is made to run off, with a constant stream of water introduced for the purpose. The stamps are of the usual description: the bars are of wood, between five and six inches square, fastened by a tail to a cast-iron head, of about 280 lbs. weight. The stamp-chest is open behind, so that, as the ore is pounded, it slips away from under the stamp-heads by its own gravity, along an inclined plane with a stream of water. The rolls are similar to those for other ores; generally, they consist of two pairs of smooth cylinders, turning simultaneously in opposite directions. Above the upper pair is a hopper, which discharges down between them, by means of a particular mechanical contrivance, the ore which is brought to it by waggons; these waggons advance upon a railway, and empty their contents into the hopper through a trap-hole. Below the hopper is a small iron bucket, which receives the ore, is shaken, and throws it continually upon the rolls by the constant jolts given to it by a crank-rod. This bucket is so contrived, that too much ore can never fall upon the rolls and obstruct their even movement. A small stream of water is often led into the bucket, spreading over the rolls and preventing them from heating. After the ore is reduced to powder, it next undergoes the very important operation of washing.

This operation is carried on under very advantageous circumstances compared with the similar operation with most other metals, in consequence of the high specific gravity of the cassiterite, which enables the washing to be profitably applied, even when the ore contains only 0·5 to 1·0 per cent. of tin. The ore is washed either in a *buddle* and *tossing-tub* or *dolly* (in the German *chest* or *rack*), or in the *trunking-box*, which are employed according to the different conditions of the pulverised ore. As the process of washing does not differ materially from that adopted for the ores of other metals, it is unnecessary to enter into a description of the various machines employed in Cornwall. The rich products of the washings consist principally of stannic oxide and the heavy metalliferous ores, such as arsenides, disulphides of iron, and wolfram mixed with sands and slimes. The sands from several of the tin-mines, after washing, have a white metallic colour, arising from the presence of arsenical pyrites (*mispickel*); the workmen call them *tin-white*. After the ores are washed, they are removed to the *burning-house*, to be calcined in a reverberatory calciner, which differs but slightly from that employed for copper-ores, excepting that it is smaller, and has only one door. The chimney generally leads to flues, in which the arsenious acid is condensed. At Par Consols the calciners have the following dimensions:—

The bottom, from the bridge to the front-door, is 7 ft. 4 in. long, 5 in the centre, 18 in. wide at the front-door, 8 in. high over the bridge, 16 in. in the centre, and 10 in. high at the sides. The ores are charged in the usual manner from a bin or hopper, the calcine-man extending them first over the surface near the bridge. They are rabbled every 20 or 30 minutes, according to the nature of the ores; and are divided into three heaps across the furnace, to expose their sides to the direct action of the heat. When some bright points are seen on the surface of the ores, and there is no longer any escape of white fumes, the work is finished. At the commencement of the calcination, only a moderate heat is applied, which is gradually increased until the sulphur (from the sulphides of iron, &c.) is nearly expelled. When the operation is conducted carelessly, and the heat applied too rapidly, a fusible sulphide of tin is formed, and the mass agglutinates, which is termed kerming: if this accident should happen, it is necessary to grind the ores over again.

When the charge is sufficiently calcined, it is removed from the calciner, and exposed in small heaps to the action of the atmosphere for a few days, to promote the oxidation of any remaining sulphides into sulphates. When thus oxidised, it is thrown into a large tub filled with water, stirred with a wooden rake, and left to settle, by which means the sulphates of iron and copper are dissolved. The water is afterwards transferred into a large tank, and the copper which may be in the solution is recovered by precipitation with metallic iron. The ore thus calcined, oxidised, and lixiviated, is washed once more on the rack-table, and the lighter parts removed. The heaviest parts necessarily contain the most metal, and are sold to the smelters under the name of black tin. That which remains in the middle of the table, being much mixed with wolfram, is called mock-lead, and sent once more to the stamps to be crushed and washed, after which it is sold as black tin.

The rotary calciners calcine well, and do much work; but they must be put in motion either by water or steam-power, and the cost of their erection is much greater than that of the ordinary reverberatory calciner, which can be put up for about £30.

The usual cost of calcining, per ton of black tin, is:

	s.	*d.*
For labour	4	0½
1714 lbs. of coal, at 13*s.* per ton . .	9	6
	13	6½:

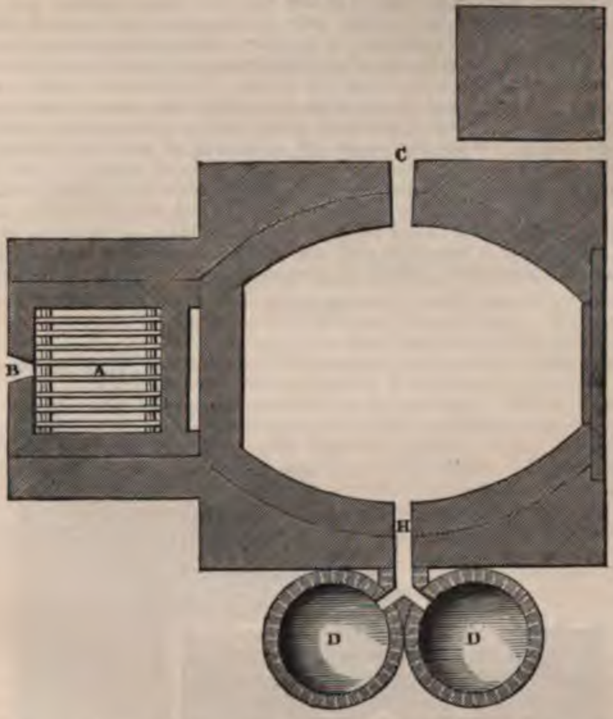
to which must be added the wear-and-tear of utensils, &c. Some calculate that the average cost is greater, amounting to 20*s.* per ton: from this is to be deducted, however, the value of a large quantity of arsenious acid obtained. The mean yield of tin-ores prepared in Cornwall may be estimated at 2 per cent.—that is to say, 50 tons of ore will give 1 ton of black tin. The cost of the mechanical preparation of the ores varies greatly in proportion to their yield, the hardness of the gangue, &c., but those of the usual produce and hardness may be reckoned at 4*s.* 10*d.* per ton of ores, or about £12 per ton on black tin. There are, however, many ores which do not contain more than 0·5 per cent. of metal, but they are easily dressed, as the grain is large and pure, and they require no calcining: their cost of calcination may be calculated as follows:

	s.	*d.*
Rugging and spalling	1	0
Stamping	0	4
Washing	1	0
	2	4 per ton of ore,

equal to £23 6*s.* 8*d.* per ton of black tin. This estimate does not take account of the loss in washing, which is supposed to average fully 20 per cent., and in the assay, which is less than the actual product.

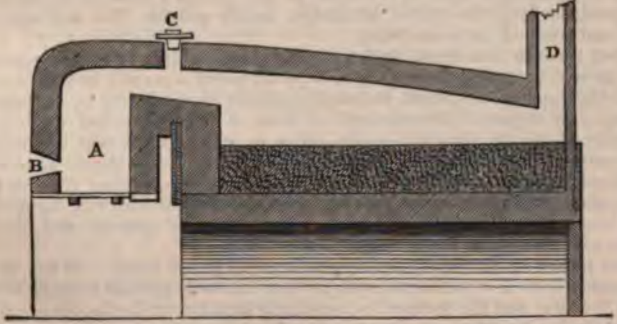
The smelting of the black tin is effected in reverberatory furnaces. When only an impure metal is required, it undergoes two different processes—first, in a reduction furnace, and then in a refining furnace. When a very pure tin is wanted, called *grain-tin*, the stream-tin is fused in a blast-furnace supplied with charcoal. It will be seen (by *figs.* 817, 818, and 819), that the reverberatory furnaces employed, are not essentially different from those for copper, except in the addition of the two round basins (*fig.* 817), D D, into which the melted tin is drawn off and ladled into moulds.

Fig. 817.



When the furnace is properly heated, it is charged with about a ton of calcined ore, which is intimately mixed with fine charcoal or anthracite-coal, to the amount of about 20 per cent. of its weight; also with some slaked lime or fluor-spar as a flux. When the charge is let down, the aperture C (*fig.* 818) in the roof of the bridge is opened, which permits the escape of fumes. The heat of the furnace is at first gently raised, for if it were too great, the tin-oxide would unite with the quartz of the gangue, and form a very difficultly decomposible silicate. The charge is allowed to heat for

Fig. 818.

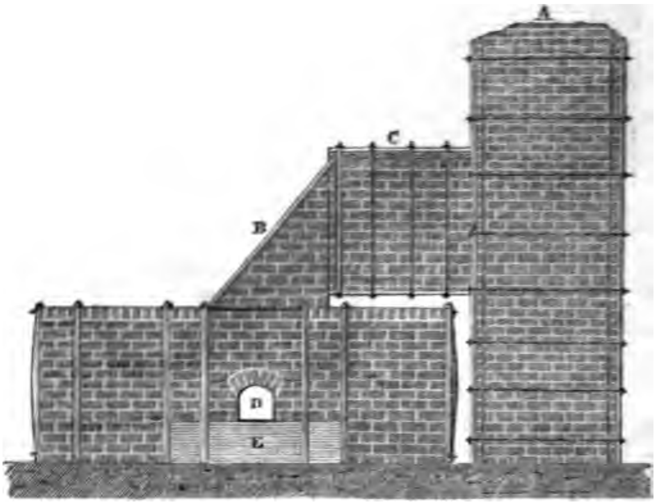


six or eight hours, when the door is opened, and it is thoroughly stirred with an iron rabble, to effect the separation of the metal and the slag. After waiting a short time to allow the metal to subside, the slag or scoria which floats on the surface is skimmed off with a skimming rabble and preserved; the upper part of the slag is poor in metal, but the lower is rich; it is therefore re-smelted. When the metal is perfectly skimmed, the tap-hole, which is stopped with a plug of dry wood at the side of the furnace, is opened, and the tin allowed to flow into the circular basins.

The tin thus reduced is by no means pure; it is necessary that it should undergo the refining process, which is performed by liquation and refining proper (lixiviation). Liquation is accomplished in a reverberatory furnace very similar to that in which the smelting is effected; but it is provided with a more sloping bottom, similar to that for refining copper. The pigs of tin are piled up in the [illegible] close to the bridge, and the tin, when moderately heated, gradually melts, and flows down into the refining-basin made in the bottom. When the blocks are exhausted of pure tin, skeletons of the pigs remain as a refractory residuum, consisting chiefly of oxides of iron and other foreign metals. More pigs are placed over the remains of the first, and the metal is then run from the furnace into a large iron pan or kettle, which holds about five tons.

The next process is *refining proper, or lixiviation*.—The kettle or refining-basin is placed over a fire-grate, and heated so as to preserve the metal in a fluid state. Into this metal bath, billets of greenwood are plunged, and set in a rotary motion by a machine called a *gibbet*, placed over the kettle: the disengagement of gas from the wood causes a constant ebullition in the tin, and a froth on the surface, which is composed chiefly of the oxides of foreign metals and tin; this is skimmed off the surface, and reserved for re-smelting.

Fig. 813.



In about three or four hours, the boiling is finished: the greenwood is removed, and the tin allowed to settle. On cooling slowly, the metal separates into different strata, of which the upper is the purest, the middle slightly charged with foreign metals, and the lowest very impure. After a couple of hours, it is gently ladled out into moulds. The quality of the tin depends on the order in which it has been ladled; the first blocks contain, of course, the purest metal, and the last are so impure as to require to be again subjected to liquation and refining. The whole operation requires from five to six hours, including from one to two hours for the subsidence of the metal. The moulds into which the tin is cast are generally made of granite, and are of a size sufficient to contain three hundredweight of black tin.

Tin-ore melted in the blast-furnace produces the purest metal. When the furnace is thoroughly heated, it is charged with ore and charcoal, damped to cause an adheison between the two, and the furnace is constantly kept full while the operation is going on. The tin is allowed to run into the first basin, and then into the second, where it is left to settle for some time. The tin in the metallic bath falls into strata similar to the refining furnace, the impure part settling to the bottom, which is again

Grain-tin is formed from the finest blocks; these are heated to nearly melting-point, when they become brittle; they are then dropped from a considerable height; the metal is thus broken, and forms elongated grains or tears.

The reverberatory furnace consumes about two tons of coal for one ton of metal; the blast-furnace about thirty-one hundredweight of charcoal for one ton of metal.

It is very difficult to find out the exact loss of metallic tin in smelting by the reverberatory and blast-furnaces. It has, however, been found that black tin, which gave 73 per cent. of tin by assay, yielded 66·5 per cent. of pure tin when smelted and refined, leaving a large quantity in the state of silicate, most of which, no doubt, could be recovered. In the blast-furnace the loss is considered to be about 15 per cent.

Properties of Tin.—The tin of commerce is never pure; the metal from Banca contains, perhaps, the smallest amount of impurity. Tin is generally associated with small quantities of arsenic, lead, iron, copper, and occasionally tungsten, manganese, antimony, zinc, bismuth, and molybdenum. To obtain it chemically pure, the tin of commerce is granulated and dissolved in strong hydrochloric acid; a small quantity of water is cautiously poured into the solution, so as to form two strata; and a plate of tin is then introduced, traversing the two liquids. After some time, crystals of pure tin are deposited upon the plate, owing to the feeble galvanic current which is excited. Or tin may be digested in nitric acid, the white insoluble residue (metastannic acid) digested in dilute hydrochloric acid, and the resulting powder reduced by charcoal.

Tin is a white metal, having however a peculiar yellowish tinge. When warm, it emits a characteristic smell, and a bar, when bent, gives a singular crackling sound (*cri d'étain*), owing to the interior crystals breaking against each other. It is soon tarnished by the air of large towns, owing probably to a film of sulphide, as it is not sensibly affected by the combined presence of air and moisture. Tin, with the exception of lead and thallium, is the least tenacious of the well-known metals. A wire $\frac{1}{15}$ of an inch in diameter will support only about 31 pounds: a bar, a quarter of an inch in diameter, will not support more than 294 pounds weight. The malleability of tin is very considerable; it is expanded, by combined hammering and heating, into sheets or leaves called **tinfoil**, barely $\frac{1}{1000}$th part of an inch in thickness. It is tinfoil that is laid upon the back of glass mirrors, and there amalgamated with mercury, forming what is called the **silvering**.

Tin can be easily obtained in crystals, in the same manner as bismuth. The best method is to fuse some pounds of the metal, and, when it is nearly solidified, to pierce the centre of the mass with a stick of incandescent charcoal, and pour off the portion which still remains liquid; fine crystals of tin are then found upon the sides of the interior. Tin, indeed, has a remarkable tendency to crystallise, as may easily be shown by washing the surface of the metal with warm, diluted, nitro-hydrochloric acid, when it becomes covered with a mass of crystalline forms, having a very beautiful appearance something like watered silk, and formerly much used, under the name of *moirée metallique*, for the manufacture of workboxes, tea-caddies, &c. The appearance is caused by the unequal reflection of light by the facets of the crystals exposed to the action of the acid. Louis Vallet, in 1817, obtained a patent for the production of these crystals, or, as he expressed it, for the manufacture of a new ornamental surface of metal or metallic composition. The surfaces of tin, or of metals coated with tin, are washed with a mixture of 10 pts. of sulphuric acid diluted with five times its bulk of water, together with 1 pt. of nitric acid diluted with its own weight of water. In the following year (1818), Mr. M. Isambard Brunel obtained a patent for a somewhat similar application of acids on the surface of tin. The process is thus described: "A new species of tinfoil, capable of being crystallised in large, varied, and beautiful crystallisation." A sheet of tin or tinfoil is laid evenly upon a flat plat of metallic or vitreous substance, which may be heated from below by a bath of melted alloy, as of two-thirds of tin and one-third of lead: heat is then applied, by means of common gas-jets and flexible tubes, to those parts to which it is desired to give an ornamental crystalline conformation. Sulphuric acid diluted with 5 pts. of water, and nitrous (?) acid diluted with 1 pt. of water, are mixed in the proportion of 10 pts. of the former to 1 pt. of the latter, and applied by a brush to the surface of the tin; it is then washed, and may be varnished or japanned in the usual way.

The specific gravity of tin is 7·29, and is not sensibly increased by rolling. That of the crystals was found by **Miller** to be 7·177: according to **Deville**, the specific gravity of slowly-cooled tin is 7·373; that of tin rapidly cooled, by pouring into water, 7·239. Its cubical expansion for 1° C. (between 9° and 72°) is 0·000070. (**Kopp.**)

Tin melts at 222° (**Crichton** and **Rudberg**), at 230° (**Kuppfer**), at 237·2° (**Person**). Its specific heat in the solid state is 0·0562, in the liquid state 0·0637; its latent heat of fusion, between 250° and 350°, is 14·252 (**Person**). It boils at a white heat. It has but a small heat-conducting power (according to Calvert = 422, that of silver being 1000). It takes a fine polish, and has then but little radiating power: hence vessels of polished tin are well adapted for keeping liquids warm.

Tin does not oxidise at ordinary temperatures in the air, even when moist, and but very slightly in water, retaining its metallic lustre for a long time: hence iron which is to be exposed to the air is often tinned, to prevent it from rusting. When tin is fused in the air, its surface becomes covered with a thin grey film, containing both protoxide and dioxide of tin. If the film be removed, it is again formed, and if this grey powder be continuously heated, it becomes white. It is used for polishing plate in the same way as *putty-powder*, which is obtained by the action of nitric acid upon the metal.

If tin be kept at an ordinary red heat, it gives out vapours, but they have little tension, and there is but small loss of weight; at a strong white heat, it burns in the air with a bright flame. At a full red heat it will decompose steam, with evolution of hydrogen.

Strong *nitric acid* of specific gravity 1·5 does not act upon tin, the metal even preserving its characteristic brilliancy; but if the acid is diluted, it attacks the metal with extreme violence, the tin being entirely converted into metastannic acid.

Tin dissolves slowly in dilute or cold *hydrochloric acid*, but rapidly when the latter is hot and concentrated, evolving hydrogen-gas, and yielding dichloride of tin. Dilute *sulphuric acid*, when heated, attacks tin slowly, with emission of hydrogen, but the hot concentrated acid acts more energetically, with production of sulphurous acid. Fused *nitre* and the *hydrate of potassium* and *sodium*, at high temperatures, act upon tin. It combines directly with *sulphur*, *phosphorus*, *chlorine*, *iodine*, &c., and forms alloys with many *metals*, particularly with *copper*, to which it gives a hardness approaching to that of steel.

Tin in a state of fine division is violently acted upon by *chloride of sulphur*, the heat evolved being so great that the sulphur-compound (which must be returned) passes over with the tetrachloride of tin. (Wöhler, Ann. Ch. Pharm. lxxiii. 374.)

Compounds of Tin.—Tin forms chiefly two classes of compounds: namely, the stannous compounds, in which it is diatomic—*e.g.*, $SnCl^2$, SnO. SnS, $Sn(SO^4)$, &c.; and the stannic compounds, in which it is tetratomic—*e.g.*, $SnCl^4$, SnO^2, SnS^2, $Sn(SO^4)^2$, &c. There are also a sesquioxide, Sn^2O^3, a sesquisulphide, Sn^2S^3, and several compounds of tin with alcohol-radicles, in which it is triatomic. F. F.

TIN, ALLOYS OF. Tin unites with most other metals, forming, in many cases, hard ductile alloys. Small quantities of tin are often sufficient to impart peculiar properties to an alloy.

Many of the alloys of tin have been already described in connection with the other metals. For Matthiessen's determinations of the specific gravities of tin-alloys, see Pogg. Ann. cx. 21; Jahresb. 1860, p. 111; also the article METALS in this Dictionary (iii. 943).

Tin and Antimony (i. 317).—According to Chaudet, 10 pts. tin and 1 pt. antimony form a perfectly ductile alloy.

Tin and Arsenic unite easily when heated together, forming a hard, brittle, laminar mass, less fusible than tin. When the proportion of arsenic is large, the alloy is insoluble in hydrochloric acid; with a smaller amount, it dissolves, with evolution of arseniotted hydrogen, leaving an alloy richer in arsenic. (Soubeiran.)

Tin and Bismuth.—An alloy of 177 pts. (3 at.) of tin and 213 pts. (2 at.) of bismuth, when cooled from a state of fusion, exhibits but one solidifying-point; inasmuch as it first cools regularly down to 143°, and then remains at that temperature for a considerable time, till the latent heat, set free in the solidification of the alloy, has had time to escape. But all other alloys of these metals likewise exhibit a higher solidifying-point, the excess of one or the other metal, or, rather, another definite alloy containing an excess of one of the two metals, solidifying first, and afterwards at 143°, the hitherto fluid alloy containing Sn^3Bi^2. The higher solidifying-point, or point of separation, is 190° for Sn^4Bi, 160° for Sn^2Bi, 150° for $SnBi$, 170° for Sn^2Bi^3, and 190° for $SnBi^2$. (Rudberg, Pogg. Ann. xviii. 240.)

a. 40 pts. tin to 1 pt. bismuth: perfectly ductile; the addition of 1 pt. of lead diminishes its extensibility.—*b.* 25 pts. tin to 1 pt. bismuth: slightly ductile (Chaudet).—*c.* 8 pts. tin to 1 pt. bismuth: melts at 199° (Lewis).—*d.* 3 pts. tin to 1 pt. bismuth: pulverisable; of dull grey fracture, and specific gravity 7·776; gives up all its tin, with a small quantity of bismuth, to heated hydrochloric acid (Chaudet).—*e.* 2 pts. tin to 1 pt. bismuth: melts at 166° (Lewis).—*f.* 236 pts. (2 at.) tin to 213 pts. (1 at.) bismuth: specific gravity = 8·085 (Regnault).—*g.* 1 pt. tin to 1 pt. bismuth: perfectly brittle; pulverisable; of fine-grained fracture; [illegible] gravity = 8·345 (Chaudet). Melts at 138° (Lewis). Expands stro[illegible]ifying (Marx). With hydrochloric acid it behaves like *d* (Chaudet, A[illegible][2], v. 142).—

h. 177 pts. (3 at.) tin to 213 pts. (2 at.) bismuth: melts between 131° and 137° (Döbereiner, Kastn. Arch. iii. 90).—*i.* 118 pts. (1 at.) tin to 213 pts. (1 at.) bismuth: specific gravity = 8·759. (Regnault.)

236 pts. (2 at.) tin to 213 pts. (1 at.) bismuth, and 129 pts. (1 at.) antimony, form an alloy of specific gravity 7·883 at 20°. (Regnault, Ann. Ch. Phys. [2], lxxvi. 136.)

Respecting the alloys of tin, bismuth, and lead, see i. 591, and iii. 536.

Tin and Cadmium.—The alloy Sn^2Cd melts at 173·8°. (Rudberg.)

Tin and Cobalt form a somewhat malleable alloy.

Tin and Copper (see COPPER, ii. 43). Rieffel (Compt. rend. xxxvii. 454; Jahresb. 1853, p. 376) gives the following list of alloys, which he regards as chemical compounds of copper and tin:—

	Cu.	Sn.	Colour.
$CuSn^{48}$	1·11	98·89	White, more or less approaching to that of tin.
$CuSn^{24}$	2·19	97·81	
$CuSn$	34·98	65·02	Iron-grey.
$SnCu^{24}$	92·81	7·19	Golden-yellow.
$SnCu^{48}$	96·27	3·73	Orange-yellow.
$SnCu^{72}$	97·48	2·52	Yellowish-rose.
$SnCu^{96}$	98·10	1·90	Rose.

In the alloy SnCu, which crystallises in large steel-grey laminæ, hard, bulky, and melting at about 400°, the properties of both the constituent metals are said to be nearly masked; the other alloys exhibit the characteristics of the predominant metal. The formation of all these compounds is attended with condensation.

The alloy $CuSn^2$ (21·3 pts. copper and 77·6 pts. tin) has been found, as a furnace-product, in white six-sided prisms, of specific gravity 7·53 (Miller, Pogg. Ann. cxx. 55).—Another furnace-product, from Schlackenwald, Cu^3Sn^7 (18·9. pts. copper and 80·8 pts. tin), forms semi-malleable six-sided prisms, of specific gravity 6·994, having a white colour, with golden-yellow tarnish. (Rammelsberg, *ibid.* cxx. 54.)

According to Calvert and Johnson (Jahresb. 1858, p. 111), the heat-conducting power of Sn^5Cu = 396; of SnCu = 415 (silver = 1000).

Calvert, Johnson, and Lowe (Jahresb. 1861, p. 1) have determined the relative expansions of several alloys of copper and tin to be as follows: SnCu = 138·1; SnCu = 118·1; $SnCu^4$ = 111·8; $SnCu^{15}$ = 98·3; $SnCu^{25}$ = 105·0.

Alloys of tin with copper and antimony constitute several varieties of Britannia-metal, also Deurance's alloy for fractional bearings (ii. 46).

Tin and Gold.—Tin considerably diminishes the extensibility of gold. The alloy of 11 pts. gold and 1 pt. tin is pale-yellow, fine-grained, only slightly malleable, and has a specific gravity of 17·307 (Hatchett). Alloys of tin and gold are, for the most part, easily crystallisable. The compounds SnAu and Sn^3Au^2 do not, however, appear to crystallise; but on addition of more tin, in such proportion as to form the compound Sn^2Au, the fused mass separates into a less fusible portion, having a vitreous fracture, and an easily fusible crystalline mass. (Matthiessen and v. Bose, Phil. Trans. 1860, p. 170.)

Iridium melts with 4 pts. of tin, at a bright-red heat, to a dull-white, hard, crystallisable alloy (Berzelius). The alloy $IrSn^2$ (45·4 pts. iridium and 54·6 pts. tin) crystallises in cubes, which are not altered by nitromuriatic acid.

Respecting the alloys of tin with iron, lead, and mercury, see iii. 370, 534, 870; with palladium and platinum, iv. 327, 667.

Tin and Nickel form a hard brittle alloy.

Tin and Potassium melt easily together. Stanniferous potassium, obtained by igniting tin or stannic oxide with cream of tartar, is brittle, and decomposes water.

Tin and Rhodium form a black, shining, crystalline mass, containing RhSn. 47·3 pts. tin, 32·0 platinum, 12·5 iridium, and 1·9 rhodium, form a crystallisable alloy, $(PtIrRh)^2Sn^3$, which is not altered by hydrochloric acid.

Tin and Ruthenium.—When 1 pt. of ruthenium is fused with 10 to 15 pts. tin in a crucible lined with charcoal, and the cooled mass is treated with hydrochloric acid, a crystallisable alloy, $RuSn^3$, remains, containing 33 pts. ruthenium to 67 pts. tin.

Tin and Silver (p. 287).

Tin and Sodium may be alloyed together by direct fusion, or by igniting tin with soda-soap. The alloy resembles that of tin and potassium.

Tin and Zinc. See ZINC.

TIN, BROMIDES OF. *Stannous bromide*, $SnBr^2$, is formed by heating metallic tin in hydrobromic acid gas, or with mercuric bromide. It is a greyish-white, shining, crystalline mass. It dissolves in water, and the resulting solution, as well as that obtained by dissolving tin in aqueous hydrobromic acid, yields, on evaporation, [illegible] crystals. Stannous bromide melts, at a high temperature to [illegible] the air, it gives off stannic bromide and leaves stannic [illegible]

[illegible] $SnBr^4$, is produced, with incandescence, when tin or stannous [illegible] vapour. It is a white crystalline mass, of specific gravity [illegible] and sublimes in needles. It dissolves in water [illegible] temperature; melts under oil of vitriol without sensible [illegible] it to stannic hydrate, with separation of bromine.

[illegible] is formed by the action of bromine on stannous oxide.

[illegible] forming the compound $SnBr^4.(C^2H^5)^2O$, in deli[illegible] water before dissolving in it, and are easily disin[illegible] yielding hexagonal prisms of stannous bromide. [illegible]

TIN, BUTTER OF. [illegible].—An obsolete name for hydrated tetr[illegible] Gmelin's Handbook (v. 84), for the anhydrous di[illegible]

TIN, CHLORIDES OF. Three chlorides of tin are known, corresponding to [illegible] and $SnCl^4$.

Dichloride, or Stannous Chloride, $SnCl^2$, (commonly called *Protochloride of Tin*, and represented, according to the old atomic weight of tin, by the formula SnCl.) — [illegible] is prepared:—1. By gradually heating tin, or tin-amalgam, [illegible] or with at most 2 pts. of mercuric chloride, the mercury [illegible]. 2. By heating tin in hydrochloric acid gas, hydrogen being set free. — 3. By heating hydrated stannous chloride in close vessels, whereupon, when the heat is gradually raised to redness, and the receiver changed, the anhydrous chloride passes over after the water. Capitaine (J. Pharm. xxv. 552) gently heats [illegible] in a capacious crucible (to prevent frothing over), as long as it gives off water and sulphuric acid; pours the mass, as soon as it is [illegible] tranquil fusion, into a small crucible; then pounds it up coarsely, and distils it from a [illegible] glass retort. The first portions of stannous chloride which pass over are perfectly pure; the last portions contain a small quantity of iron, from which they may be freed by a second distillation.

Stannous chloride is translucent, almost pure white (frequently grey), with a fatty lustre and conchoidal fracture; soluble in water and in alcohol. It melts at 250° to an oily liquid, which penetrates the crucibles and makes them crack; boils at a heat near redness, but always with some degree of decomposition. When cooled after fusion, it remains liquid for a long time, but afterwards becomes syrupy and solidifies. When heated to bright redness, it gives off tetrachloride of tin, and afterwards unaltered dichloride, leaving a black shining mass, which dissolves in aqueous hydrochloric acid with evolution of hydrogen-gas, and forms a solution of stannous chloride (A. Vogel, Schw. J. xxiv. 66). When heated to the boiling-point, it passes over in company with tetrachloride of tin, and leaves yellow, earthy, stannous oxychloride, $SnCl^2.SnO$ (Capitaine).—When heated with sulphur, it yields tetrachloride and disulphide of tin: $2SnCl^2 + S^2 = SnCl^4 + SnS^2$ (Proust).—When heated in the air, or with nitre, chloride of potassium, or mercuric oxide, it gives off tetrachloride of tin, and leaves stannic oxide. At ordinary temperatures, it does not suffer much alteration by exposure to the air: in the course of three weeks, however, it becomes somewhat disintegrated, but still dissolves completely in water.

Stannous chloride absorbs dry *ammonia-gas*, and when heated with it, forms the compound $SnCl^2.NH^3$.

Hydrated stannous chloride, commonly called *tin-salt*, is obtained by dissolving the anhydrous chloride in water, or by the solution of metallic tin in hydrochloric acid.

The preparation on the large scale is performed in copper vessels, which, so long as any portion of tin remains undissolved, are not attacked by the acid. If granulated tin be covered with hydrochloric acid, then the acid poured off, and the tin exposed to the air—afterwards the acid poured on again, and so on alternately—the tin takes up oxygen from the air, whereby it becomes heated, and dissolves much more quickly than by the simple action of the acid (Berard). In the preparation of *tin-salt* on the large scale, Nöllner (Arch. Pharm. lxiii. 120) recommends that the hydrochloric acid, as it is evolved from the retorts, be made to act directly upon granulated tin contained in stoneware receivers adapted to the retorts, and that the concentrated solution of tin-salt thus formed be aft[illegible] tinned pans, with addition of granulated tin.

The solution, when e[illegible] rent, colourless prisms (monoclinic accor[illegible] metallic taste. According to Be[illegible] ording to Henry, they contain $SnCl^2.2H^2O$. The crystals, when heated, evolve water and hydrochloric acid containing a small quantity of tin, and leave stannous chloride and oxide. Cold oil of vitriol separates from them but a small quantity of hydrochloric acid; heated oil of vitriol separates hydrochloric acid—together with small quantities of stannous chloride, sulphurous acid, and sulphuretted hydrogen (the two latter substances partly decomposing each other, and yielding a precipitate of sulphur)—and forms stannic sulphate. (A. Vogel.)

The pure crystals of tin-salt dissolve completely in a certain quantity of deaërated water, a litre of the solution, saturated at 15°, having a specific gravity of 1·827, and containing 1,333 grms. of stannous chloride to 494 grms. of water (Michel and Kraft). A larger quantity of water produces partial decomposition, hydrochloric acid being dissolved, and a hydrated stannous oxychloride, $Sn^2OCl^2.2H^2O$, being deposited in the form of a milk-white powder:

$$2SnCl^2 + H^2O = Sn^2OCl^2 + 2HCl.$$

The clear neutral solution also becomes turbid on exposure to the air, likewise from formation of oxychloride, while stannic chloride remains in solution:

$$3Sn''Cl^2 + O = \overset{\text{iv}}{Sn}{}^2OCl^2 + Sn^{iv}Cl^4.$$

In either case the decomposition may be prevented, and the solution kept clear, by addition of hydrochloric or tartaric acid, or of sal-ammoniac, with which stannous chloride forms a double salt not decomposible by water or by exposure to the air. The crystals of tin-salt likewise decompose on exposure to the air in the manner above mentioned.

A *hydrated stannous chloride*, containing $SnCl^2.4H^2O$, is obtained in needle-shaped deliquescent crystals, melting at 50°, by dissolving stannous oxide in an equivalent quantity of stannic chloride, and evaporating, the mother-liquor then retaining stannic oxide dissolved in stannic chloride:

$$2SnO + 2SnCl^4 + 8H^2O = 2(SnCl^2.4H^2O) + SnO^2 + SnCl^4.$$

Stannous chloride is a powerful deoxidising agent, reducing *gold-*, *silver-*, and *mercury-salts* to the metallic state; converting *ferric*, *manganic*, and *cupric chlorides* into ferrous, manganous, and cuprous chlorides respectively; the *trioxide of chromium* (chromic anhydride) into sesquioxide; *tungstic* and *molybdic anhydrides* into the corresponding blue oxides; the higher oxides of *lead*, *bismuth*, &c., into lower oxides, and *indigo-blue* into indigo-white.—*Arsenic acid* forms with stannous chloride a precipitate consisting, according to Schiff, of stannic arsenite, $2SnO^2.As^2O^3$; an excess of stannous chloride, however, reduces the arsenic acid to metallic arsenic. Stannous chloride also reduces *nitric acid* to nitric or nitrous oxide, *hypochlorous acid* to chlorine, &c. With *sulphurous acid* in presence of hydrochloric acid, it forms stannic sulphide together with stannic chloride, a reaction which may be used for the detection of sulphurous acid (p. 541):

$$6SnCl^2 + 8HCl + 2H^2SO^3 = SnS^2 + 5SnCl^4 + 6H^2O.$$

Stannous chloride is often used as a reagent in volumetric analysis for the estimation of indigo, &c. Tin-salt is extensively employed as a mordant in dyeing and calico-printing, sometimes also as an antichlore.

Stannous chloride forms crystallisable double salts with several other metallic chlorides.

Ammonio-stannous Chlorides.—α. The compound $2NH^4Cl.SnCl^2$ is formed by heating tin-filings with sal-ammoniac, more easily, however, by evaporating a mixed solution of the component chlorides; the crystals thus obtained are sometimes anhydrous, sometimes they contain 2 at. water (Graham). Apjohn obtained octahedral crystals, $2NH^4Cl.SnCl^2.H^2O$, which were permanent in the air, had an acid reaction, and dissolved in water, forming a solution which became cloudy on boiling. Rammelsberg obtained rhombic crystals having the same composition.—β. The salt $4NH^4Cl.SnCl^2.3H^2O$ forms tufts of needles permanent in the air, but decomposed by water. (Poggiale, Compt. rend. xx. 1180.)

The *barium-* and *strontium-salts* are represented by the formulæ $BaCl^2.SnCl^2.4H^2O$ and $SrCl^2.SnCl^2.4H^2O$.

Potassio-stannous Chlorides.—α. The salt $2KCl.SnCl^2$ is prepared like the corresponding ammonium-salt, and is said to form anhydrous crystals, as well as crystals with 1, 2, and 3 at. water. The monohydrate forms rhombic crystals. (Marignac, Compt. rend. lv. 650.—Rammelsberg, Krystall. Chemie, p. 211.)

A compound of *stannous chloride* with *potassio-stannous sulphate*, $SnCl^2.4SnK^2(SO^4)^2$, separates from a mixture of the hot concentrated solutions of stannous chloride and potassium-sulphate, in small, shining, hexagonal crystals, which may be recrystallised from water without decomposition.

Sesquichloride of Tin, or *Stannoso-stannic Chloride*, $Sn^2Cl^6 = SnCl^2.SnCl^4$.

—This compound, known only in solution, is produced by dissolving stannoso-stannic hydrate in hydrochloric acid, in a vessel from which the air is excluded. The solution reacts like a mixture of stannous and stannic chlorides.

Tetrachloride of Tin, or **Stannic Chloride**, $SnCl^4$.—This compound was known to the older chemists, having been mentioned by Libavius, in 1605, under the name of *Liquor s. Spiritus argenti vivi sublimati* (from the mode of preparation with mercuric chloride); afterwards it was commonly called *Spiritus fumans Libavii*, sometimes also *Fumigatorium perpetuum joviale*.—The anhydrous tetrachloride may be obtained by distilling stannic sulphate with sodium-chloride, or by distilling the hydrated tetrachloride with oil of vitriol. It is usually prepared by distilling a mixture of 1 pt. tin-filings with 4 or 5 pts. mercuric chloride, or by heating tin-filings or stannous chloride in dry chlorine-gas, the tetrachloride then collecting in the receiver, which must be kept cool. In preparing it by the last-mentioned method, the free chlorine must be removed by agitating the distillate with tin-filings, and then rectifying it.

Stannic chloride is a colourless mobile liquid, of specific gravity 2·267 at 0°. It fumes strongly in moist air; boils at 115° (at 120° according to Duma, at 112° according to Andrews). Vapour-density, according to Dumas' determination, = 9·20; by calculation = 9·01. Its specific heat for the unit of volume is 0·8639; for the unit of weight, 0·0939 (Regnault). It does not conduct electricity. It is highly caustic, decomposes alcohol, with formation of ether; in contact with oil of turpentine, it produces great heat, sometimes setting fire to the turpentine. It converts mercury into calomel. Strong nitric acid decomposes it, with formation of metastannic acid; heated in sulphydric acid gas, it is partially decomposed, with formation of stannic sulphide.

Hydrated Stannic Chloride.—The anhydrous tetrachloride absorbs water rapidly from the air, and forms crystals of a trihydrate, $SnCl^4.3H^2O$ (Casselmann). Mixed with one-third of its weight of water, it solidifies to a soft fusible mass, called *Butter of tin*, or *Butyrum stanni*, which dissolves in excess of water, the solution yielding, by evaporation, deliquescent crystals of a pentahydrate, $SnCl^4.5H^2O$, which give off 3 at. water over oil of vitriol (Lewy, Compt. rend. xxi. 369). A solution of stannic chloride may be prepared by dissolving ordinary stannic hydrate in hydrochloric acid, by treating a solution of stannous chloride with chlorine-gas, or by mixing stannous chloride with hydrochloric acid and treating it with nitric acid. The salt generally known in commerce as nitromuriate of tin, is prepared by dissolving tin in nitromuriatic acid, which must be kept cool, and must not contain too much nitric acid—otherwise metastannic acid is likely to be produced. This solution is used in dyeing for the brightening and fixing of red colours, and is sometimes designated by the old names, "composition, physic, or tin-solution." The same solution is obtained by dissolving tin to saturation in hydrochloric acid, then adding half as much hydrochloric acid as was required to dissolve the tin, together with a certain quantity of sulphuric acid and nitre. Stannic chloride may also be prepared by oxidising stannous chloride with chlorate of potassium; and on evaporating the liquid, or the solution of stannous chloride mixed with nitric acid, the trihydrate, $SnCl^4.3H^2O$, is obtained (which, when dried in a vacuum, leaves the dihydrate, $SnCl^4.2H^2O$), while the mother-liquor contains stannic hydrate dissolved in stannic chloride. (Scheurer-Kestner, Compt. rend. l. 50.)

The solution of stannic chloride exhibits all the reactions of ordinary stannic salts (p. 810). When evaporated, it first gives off water, then stannic chloride. The concentrated solution does not alter perceptibly; but the dilute solution gradually decomposes, yielding hydrochloric acid and metastannic hydrate (p. 817), which remains behind when the hydrochloric acid is evaporated. According to Casselmann, a solution diluted to a certain point deposits ordinary stannic hydrate as well as metastannic hydrate. When stannic chloride is heated with a small quantity of water in a sealed tube, pure amorphous stannic oxide separates. (Senarmont.)

Aqueous stannic chloride easily dissolves stannous oxide, forming stannous chloride which on evaporation crystallises as a tetrahydrate, $SnCl^2.4H^2O$ (p. 807), while the liquid retains stannic hydrate dissolved in stannic chloride. When an excess of stannous oxide is dissolved in stannic chloride, the mass solidifies to a pulp of stannic hydrate, and the liquid which runs off yields, on evaporation, the dihydrate of stannous chloride, $SnCl^2.2H^2O$. (Scheurer-Kestner.)

Compounds of Stannic Chloride.—Stannic chloride unites with a considerable number of bodies, both organic and inorganic. It dissolves crystallisable (not amorphous) *sulphur*, when heated with it; also ordinary *phosphorus*, *iodine*, and other bodies, in large quantity; it mixes in all proportions with *bromine* and *carbonic disulphide*, and like the latter is a solvent for many bodies. Sulphur crystallises from the hot saturated solution in rhombic prisms. (Girardin, Compt. rend. li. 1057.)

Anhydrous stannic chloride absorbs *ammonia-gas*, forming the compound

$SnCl^4.2NH^3$, which is a white powder, sublimable without decomposition, and perfectly soluble in water after sublimation. (H. Rose.)

Vapour of *sulphuric anhydride* is easily absorbed by stannic chloride, forming a solid mass. (Rose, Pogg. Ann. xliv. 320.)

Stannic chloride also quickly absorbs *sulphydric acid gas*, giving off hydrochloric acid, and forming a stannic sulphochloride, $SnS^2.2SnCl^4$:

$$3SnCl^4 + 2H^2S = SnS^2.2SnCl^4 + 4HCl.$$

The compound obtained by perfect saturation with sulphydric acid, is a yellowish or reddish liquid, heavier than water. When heated, it gives off tetrachloride of tin, and leaves the disulphide. (Dumas.)

A compound of stannic chloride with *tetrachloride of sulphur*, $SnCl^4.2SCl^4$, is produced by the action of chlorine-gas on sulphide of tin at ordinary temperatures:

$$SnS^2 + 6Cl^2 = SnCl^4.2SCl^4.$$

It forms large yellow crystals, which melt when heated, and sublime without decomposition; they fume in the air more strongly than tetrachloride of tin.

Tetrachloride of Tin with Pentachloride of Phosphorus, $SnCl^4.PCl^5$.—When a mixture of the last-described compound with trichloride of phosphorus is moderately heated in a stream of hydrochloric acid gas, a rapid action takes place, and this compound is formed, together with other products:

$$SnCl^4.2SCl^4 + 3PCl^3 = SnCl^4.PCl^5 + 2PCl^5 + S^2Cl^2.$$

If the retort in which the action takes place is connected with a receiver surrounded with ice, a pasty yellowish mass collects in the receiver, and an amorphous white body remains in the retort. On heating the yellowish mass between 100° and 120°, disulphide of chlorine escapes, and there remains a mixture of pentachloride of phosphorus with the double chloride, identical, in fact, with the amorphous white mass in the retort. On heating this mixture to a temperature between 140° and 160°, the pentachloride of phosphorus is also driven off, leaving the double chloride, which sublimes, between 200° and 220°, in highly lustrous colourless needles, which, however, soon crumble to an amorphous powder, even when kept in close vessels. The compound fumes strongly in air, and rapidly absorbs water, being thereby converted into transparent colourless crystals containing water of crystallisation. (Casselmann, Ann. Ch. Pharm. lxxxiii. 257.)

Tetrachloride of Tin with Oxychloride of Phosphorus, $SnCl^4.POCl^3$.—Obtained by the action of oxychloride of phosphorus on tetrachloride of tin: if an excess of either substance is present, the compound separates in large isolated crystals. It has a peculiar odour, melts at 66°, boils at 180°, and distils without alteration if kept from contact with moist air. It fumes in the air, and is decomposed by water. When oxychloride of phosphorus comes in contact in a close vessel with the compound $SnCl^4.2SCl^4$, the whole dissolves, forming a yellowish liquid, from which, after a while, the compound $SnCl^4.POCl^3$ crystallises; and above the crystals there remains a yellow liquid, probably SCl^4. (Casselmann.)

Tetrachloride of Tin with Phosphoretted Hydrogen, $3SnCl^4.2PH^3$.—The two bodies unite without production of hydrochloric acid; the compound is solid. (Rose.)

Nitric oxide is abundantly absorbed by tetrachloride of tin, forming a crystallisable compound, which may be distilled, but, in contact with water or with moist air, is resolved into nitric oxide and stannic chloride (Kuhlmann, Ann. Ch. Pharm. xxxix. 319). According to Hampe (*ibid.* cxxvi. 43), nitric oxide does not act on stannic chloride except in presence of oxygen; but nitric peroxide and nitrous anhydride are absorbed by stannic chloride, forming a yellow mass, which contains stannic oxide together with a crystalline sublimable compound, $3SnCl^4.4NO^2Cl$.

With *ethylic oxide*, stannic chloride forms the compound $SnCl^4.2(C^2H^5)^2O$, crystallising in shining rhombic plates, which melt at 80°, volatilise without decomposition, dissolve in ether, but are decomposed by water.—With *ethylic oxalate* it forms a crystallisable compound, $SnCl^4.C^6H^{10}O^4$, which is also decomposed by water (Lewy, Compt. rend. xxi. 371). It also forms crystallisable compounds with several nitriles, as with *acetonitrile, propionitrile, capronitrile, benzonitrile*, &c.

Double Salts.—Stannic chloride unites with the chloride of the alkali-metals and alkaline earth-metals, forming double salts, sometimes called chlorostannates: they are prepared by evaporating the mixed solutions of the component chlorides, and some of them form well-defined crystals.

The *ammonium-salt*, $2NH^4Cl.SnCl^4$, separates, on mixing the concentrated solutions of the constituent chlorides, as a crystalline powder: from less concentrated solutions, it separates, on evaporation, in regular octahedrons or cubo-octahedrons of larger size and permanent in the air. This salt is also formed in the preparation of stannic sulphide, or mosaic gold, from tin, sulphur, and sal-ammoniac, in which case it sublimes in transparent octahedrons. The crystals dissolve in 3 pts. water at 14°. The concentrated solution is not decomposed by boiling; a more dilute solution decomposes at the boiling heat, with separation of stannic hydrate, which unites with any colouring-matter contained in the solution, so that the salt acts as a mordant. It is used in calico-printing, under the name of **pink salt**, for the production of red colours. The dry salt decomposes when strongly heated, giving off stannic chloride, and yielding a sublimate of white laminar crystals.

The *barium-*, *calcium-*, and *strontium-salts* are crystallisable, and their composition (according to Lewy) is represented by the formula $M''Cl^2.SnCl^4.5H^2O$.—The *magnesium-salt*, $MgCl^2.SnCl^4.5H^2O$, crystallises in rhombohedrons.

The *potassium-salt*, $2KCl.SnCl^4$, is prepared like the ammonium-salt, or by fusing 1 at. stannic oxide with 2 at. potassium-hydrate, and dissolving in hydrochloric acid. It crystallises in octahedrons, which are permanent in the air, soluble in water, and decomposed by heat (Bolley; Lewy).—The *sodium-salt*, prepared like the potassium-salt, crystallises in rhombic laminæ, permanent in cold, efflorescent in warm air (Bolley, Ann. Ch. Pharm. xxxix. 100). Wittstein (Repert. Pharm. lxiv. 7) obtained it in anhydrous deliquescent crystals.

TIN, CYANIDE OF. See CYANIDES (ii. 273).

TIN, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions.*—All tin-compounds, when heated on charcoal with carbonate of sodium or cyanide of potassium, yield a malleable metallic globule, without any incrustation on the charcoal. This globule, when dissolved in hydrochloric acid, gives, with mercuric chloride, a white precipitate, becoming grey when heated.

2. *Reactions in Solution.*—*α. Stannous salts.*—Stannous oxide has no acid properties, tin being basylous in all stannous salts. These salts are obtained by dissolving stannous oxide in acids, the hydrate dissolving much more easily than the anhydrous oxide. They are colourless, and, in neutral solution, are partially decomposed by water, with precipitation of a basic salt. They absorb oxygen from the air, forming stannic oxide, which is precipitated if there is not enough free acid present to hold it in solution. The reactions of stannous salts are most readily studied in the solution of the chloride. They exert a powerful reducing action, converting ferric oxide into ferrous oxide, and precipitating silver and platinum in the metallic state from their solutions.—With *mercuric chloride* a white precipitate of mercurous chloride is formed, which, if the stannous salt is in excess, is further reduced to metallic mercury.—*Trichloride of gold* produces a purple precipitate in stannous salts, consisting probably of sesquioxide of tin in combination with protoxide of gold, a test by which stannous salts may always be distinguished.—*Sulphydric acid* produces, in neutral or acid solutions of stannous salts, a brown-black precipitate of stannous sulphide, which, when gently heated with a considerable quantity of sulphide of ammonium containing excess of sulphur, is converted into stannic sulphide and dissolved; acids added in excess to this solution, precipitate yellow stannic sulphide.—*Caustic alkalis* and *alkaline carbonates*, added to stannous salts, throw down a white precipitate of hydrated stannous oxide, soluble in caustic potash or soda, but not in ammonia.—*Ferrocyanide of potassium* produces a white precipitate, soluble in hydrochloric acid. Stannous salts, heated with *sulphurous acid*, yield yellow stannic sulphide and white stannic oxide.

β. Stannic salts.—Stannic oxide in the anhydrous state is insoluble in all acids, even in nitromuriatic acid. It forms two hydrates, distinguished as **stannic** and **metastannic hydrates**, the former of which is an amorphous gummy substance, soluble in hydrochloric, sulphuric, and nitric acids, and in caustic alkalis, whereas the latter, formed from by it the action of strong nitric acid, is distinguished by its insolubility in acids, especially in nitric acid and in concentrated hydrochloric acid.

The solution of **stannic hydrate** in hydrochloric acid is identical with the aqueous solution of stannic chloride. It is distinguished from stannous solutions by not exerting any reducing action.—*Metallic zinc* and *cadmium* immersed in stannic solutions throw down metallic tin in an arborescent form.—*Sulphydric acid* and *sulphide of ammonium* throw down the yellow disulphide, soluble in alkalis and in sulphide of ammonium.—*Ammonia* throws down a white bulky hydrate, soluble, with some turbidity, in a large excess of ammonia. The presence of tartaric acid prevents the precipitation.—*Potash* throws down a white bulky hydrate (probably containing potash), easily soluble in excess.—*Carbonate of potassium* gives a white precipitate, consisting (according to Frémy) of potassic stannate, which dissolves in excess of the reagent, but separates completely after a while.—*Dicarbonate of potassium* and *sesquicarbonate of ammonium* throw down the hydrated oxide, insoluble in excess of the reagent.—*Chloride of gold* gives no precipitate with stannic salts.

Metastannic hydrate, as already observed, does not dissolve in strong hydro-
forms with it a compound insoluble in acids, but soluble in pure water.

The resulting solution is precipitated by dilute sulphuric acid, also by nitric and strong hydrochloric acid.—*Potash* throws down metastannic hydrate, soluble in excess of the alkali, and reprecipitated by excess of acid, also by the chlorides of the alkali-metals, chloride of ammonium, and sulphate of potassium. The alkaline solution of metastannic hydrate solidifies to a transparent jelly on cooling.—*Ammonia* precipitates metastannic hydrate from its solution in very dilute acid; the precipitate is insoluble in excess of strong sulphuric acid, and in tartaric acid: hence metastannic hydrate is precipitated by ammonia even in presence of tartaric acid.—*Alkaline carbonates* precipitate the hydrochloric acid solution, the precipitate being insoluble in excess of the reagent.—*Nitrate of silver* forms a white precipitate, which dissolves but partially in ammonia, leaving metastannic hydrate.—*Tincture of galls* forms, after a while, a yellowish-white precipitate.—*Stannous chloride* forms a yellowish precipitate of stannous metastannate.—*Sulphydric acid* and *sulphide of ammonium* react with metastannic in the same way as stannic solutions.

Stannic and metastannic hydrates may be distinguished one from the other by their reaction with *ferrocyanide of potassium*, inasmuch as 1 at. stannic hydrate completely precipitates 1 at. ferrocyanide of potassium, whereas metastannic hydrate does not decompose that salt.

Both stannic and metastannic hydrates react as acids, forming definite salts with bases. The solutions both of stannates and metastannates, when decomposed by acids, yield precipitates consisting of the particular modification of stannic acid contained in them, which may then be distinguished by its behaviour with hydrochloric acid, &c.

Metastannic hydrate fused with a sufficient quantity of caustic alkali, forms a stannate from which acids precipitate ordinary stannic acid.

3. *Quantitative Estimation.*—Tin is estimated in the state of stannic oxide, SnO^2, which contains 78·62 per cent. of the metal. If the tin is united with other metals in the form of an alloy, the alloy must be treated with nitric acid of specific gravity about 1·3. The tin is then converted into insoluble metastannic hydrate, while the other metals (with the exception of antimony, gold, and the platinum-metals) are dissolved by the acid. The insoluble residue must then be thoroughly washed, afterwards dried, ignited, and weighed as stannic oxide. To insure complete oxidation, the alloy should be finely divided.

When the tin is in solution in hydrochloric acid (which is its usual solvent), it may be precipitated as a sulphide by sulphydric acid, and the sulphide then converted into stannic oxide by roasting in an open porcelain crucible, a small quantity of nitric acid being added to complete the oxidation.

From solutions of stannic salts, tin may be completely precipitated as stannic or metastannic acid by *dilute sulphuric acid*. The solution is first neutralised with ammonia, so as to cause a slight precipitate; hydrochloric acid is then cautiously added till the precipitate is redissolved, care being taken to avoid any great excess of acid. This solution is then mixed with sulphuric acid. If the liquid contains ordinary stannic acid (or the corresponding chloride), it must be largely diluted to insure complete precipitation; if, on the other hand, the tin is present as metastannic acid, it will be completely precipitated by sulphuric acid from less dilute solutions. In all cases the precipitate must be left to settle for some hours, the time required being longer as the quantity of free acid present is greater. It is then to be thoroughly washed, and ignited, to convert it into stannic oxide. To ascertain whether the precipitation is complete, it is advisable to test the wash-waters with sulphuretted hydrogen.

Sulphate of sodium and *nitrate of potassium* or *ammonium* are sometimes used, instead of sulphuric acid, to precipitate tin. Sulphate of sodium does not appear, however, to possess any advantage over sulphuric acid in this respect. The nitrates may be advantageously used when the solution contains bases which form soluble sulphates.

The mode of precipitation just described is very accurate, and affords a means of separating stannic from stannous salts, the whole of the latter remaining in solution after the precipitation of the stannic oxide by sulphate of sodium. (Löwenthal.)

Another method of determining the proportions of stannic and stannous salt in a mixed solution of the two, is to divide the solution into two equal parts, convert the whole of the one into stannic salt by treatment with chlorine or chromate of potassium, and precipitate with sulphuric acid, as above; this determines the total amount of tin present. The other portion is dropped into a solution of *mercuric chloride*, and the mercurous chloride thereby precipitated is collected on a weighed filter, washed, dried, and weighed. From its weight, the quantity of tin present as stannous salt may be calculated, 2 at. mercurous chloride (471) corresponding to 1 at. tin (118), present as stannous chloride, according to the equation:

$$2HgCl^2 + SnCl^2 = 2HgCl + SnCl^4.$$

Volumetric Estimation.—Tin may be estimated volumetrically by converting a stannous into a stannic salt with oxidising solutions of known strength. One at. stannous oxide, SnO, by taking up 1 at. oxygen, is converted into stannic oxide, SnO^2: consequently, 1 at. oxygen (16) is equivalent to 1 at. tin (118). The quantity of the oxidising solution required to effect the conversion is, however, materially affected by the greater or less dilution of the solution, the greater or smaller amount of free acid present, and the quantity of oxygen dissolved in the water. **Penny** (Chem. Soc. Qu. J. iv. 239; vii. 50), and afterwards **Streng** (Ann. Ch. Pharm. xc. 411), used a solution of acid potassic chromate for the titration of tin; **Schlagdenhauffen** (J. Pharm. [3] xxxi. 96) uses manganate of potassium.

Streng mixes the acid solution of stannic chloride with a little starch-paste containing iodide of potassium, and then adds a graduated solution of acid potassium-chromate, till a blue colour is developed by the separation of iodine. The reaction takes place as shown by the equation, $3SnO + Cr^2O^6 = 3SnO^2 + Cr^2O^3$, so that 1 at. tin (118) corresponds to $\frac{1}{3}$ at. acid potassium-chromate ($K^2Cr^2O^7 = 230{\cdot}6$). Streng and Penny found that 100 pts. tin required 83·2 pts of the acid chromate; the calculated quantity is 83·4. According to **Kessler** (Pogg. Ann. xcvi. 129), the titration by this method generally gives inaccurate results, for the reasons above mentioned. According to **Mulder**, the chromic acid solution ought to be titrated with pure tin, and the process conducted as far as possible under similar circumstances. According to **Löwenthal** (J. pr. Chem. lxxvi. 484; lxxviii. 384), stannous chloride in acid solution may be more exactly titrated after addition of ferric or cupric chloride. **Stromeyer** (Ann. Ch. Pharm. cxvii. 261) oxidises metallic tin, or stannous chloride, by dissolving it in excess of ferric chloride, whereby stannic and ferrous chlorides are produced:

$$Sn + 4FeCl^3 = SnCl^4 + 4FeCl^2,$$
$$\text{and } SnCl^2 + 2FeCl^3 = SnCl^4 + 2FeCl^2.$$

The quantity of ferrous salt thus formed is determined by titration with permanganate, the ferrous salt being less susceptible to the action of free oxygen than the stannous salt—and the quantity of tin is thence determined by calculation. In the first case, 4 at. iron (224 grms.), or 2 at. oxygen added (32 grms.) correspond to 1 at. tin (118); in the latter, 2 at. iron (112) or 1 at. oxygen (16), correspond to 1 at. tin (118) or 1 at. stannous chloride (189). If the tin is in the state of stannic oxide or chloride, it must first be reduced by introducing a plate of zinc into the solution, and the precipitated tin then dissolved in ferric chloride, with addition of hydrochloric acid. If it has been precipitated from an acid solution as sulphide, this precipitate is also to be dissolved in ferric chloride, a reaction which is attended with separation of sulphur:

$$SnS^2 + 4FeCl^3 = SnCl^4 + 4FeCl^2 + S^2.$$

The solution is then to be titrated as above, 4 at. iron corresponding to 1 at. tin. If the tin has been precipitated from an alkaline sulphostannate by an acid, the precipitate consists (according to **Kühn**), not of pure stannic sulphide, but of stannic sulphydrate $Sn^{iv}H^2S^3$. The decomposition by ferric chloride then takes place as shown by the equation:

$$SnH^2S^3 + 6FeCl^3 = SnCl^4 + 6FeCl^2 + 2HCl + S^2.$$

In this case 6 at. iron are equivalent to 1 at. tin.

Lenssen (Ann. Ch. Pharm. cxiv. 113) titrates stannic chloride with *iodine* in alkaline solution. The tin or stannous salt is dissolved in hydrochloric acid in an atmosphere of carbonic anhydride, and sodio-potassic tartrate (Rochelle salt), or acid sodic carbonate, is added in excess; the solution is then mixed with starch-paste, and a titrated solution of iodine in iodide of potassium is added, till a permanent blue colour is produced. Stannic iodochloride is then formed, according to the equation $Sn''Cl^2 + I^2 = Sn^{iv}Cl^2I^2$, so that 2 at. iodine (254) correspond to 1 at. tin (118).

To determine volumetrically the relative quantities of stannous and stannic salt existing together in a solution, the liquid is first titrated directly by either of the preceding methods, whereby the quantity of tin existing as stannous salt is determined; and, secondly, after the stannic salt has been reduced to stannous salt, which gives the total amount of tin.

4. *Separation of Tin from other Metals.*—In metallic alloys tin, as already observed, may be separated from most other metals except antimony, gold and the platinum-metals, by oxidising the alloy with *nitric acid*, whereby the tin is converted into insoluble metastannic acid, while silver, copper, lead, cadmium, iron, manganese, cobalt, nickel, and zinc—and likewise bismuth, if a sufficient quantity of dilute nitric acid is used—are dissolved. Tin, alloyed with metals which form volatile chlorides, may be separated by heating the finely-divided alloy in a current of *chlorine gas*; stannic chloride then

volatilises, and may be condensed in water. This method serves to separate tin from gold and the platinum-metals, which do not dissolve in nitric acid.

Precipitation with *sulphydric acid* serves to separate tin from all metals whose sulphides are not thrown down by that reagent from acid solutions. From bismuth, cadmium, copper, lead, mercury, palladium, and silver, which are precipitated in the same manner, it may be separated by digesting the precipitate in *sulphide of ammonium* containing excess of sulphur. Stannic sulphide then dissolves, and may be precipitated by hydrochloric acid.

Sulphide of ammonium also dissolves the sulphides of arsenic, antimony, gold, platinum, molybdenum, selenium, and tellurium. The methods of separating tin from antimony and arsenic have already been fully described (i. 322, 369). From a solution of stannic chloride containing also the chlorides of gold and platinum, the latter metals may be precipitated in the metallic state by *ferrous acetate*, the tin then remaining in solution. If tin is mixed with these metals in the form of oxide or other insoluble compound, the three metals may be reduced by igniting the compound in hydrogen-gas, and the reduced alloy heated in chlorine gas, as above described.

From molybdenum, selenium, and tellurium, and from all metals which form soluble sulphates, tin, after being brought to the state of stannic chloride by treatment with chlorine or chlorate of potassium, may be separated, by precipitation as stannic or metastannic acid, with *sulphuric acid*. From barium, strontium, or calcium, it may be separated, in like manner, by *nitrate of ammonium* or *potassium*.

5. *Atomic Weight of Tin.*—Berzelius (Gilb. Ann. x. 235) found that 100 pts. tin, oxidised by nitric acid and ignited, yielded 127·2 pts. stannic oxide, SnO^2: hence the atomic weight of tin should be 117·64. Mulder (Ann Ch. Pharm. lxxii. 212) obtained, in like manner, 127·56 pts. of stannic oxide, giving $Sn = 116·1$. Dumas (*ibid.* cv. 104; cxiii. 26), on repeating this experiment, obtained, as a mean, $Sn = 118·06$; and by determining the quantity of silver required for precipitating a known weight of stannic chloride, the same chemist obtained $Sn = 118·09$. The atomic weight of tin may therefore be taken at 118°.

TIN, FLUORIDES OF. Tin forms two fluorides—viz., a difluoride and a tetrafluoride.

The *Difluoride*, or *Stannous fluoride*, SnF^2, is obtained by evaporating the solution of stannous oxide in hydrofluoric acid, and crystallises in small, shining, opaque prisms, having a sweetish astringent taste. When heated in the air, it takes up oxygen, and forms stannic oxyfluoride, $Sn^{iv}OF^2$ or $SnO^2.SnF^4$.

Ammonio-stannous fluoride.—Stannous chloride yields, with fluoride of ammonium, a precipitate composed of metallically lustrous micaceous laminæ, soluble in potash. (Unverdorben.)

The *Tetrafluoride*, or *Stannic fluoride*, has not been obtained in the free state as a definite compound, but it forms crystallisable double salts with other metallic fluorides. A solution of stannic hydrate in aqueous hydrofluoric acid coagulates like albumin when heated, but does not yield any crystals by evaporation; when evaporated in contact with the air, it gives off hydrofluoric acid, and leaves the oxyfluoride above mentioned.

The fluostannates, $2MF.SnF^4$ and $M''F^2.SnF^4$, are analogous in composition to the stannates, $M^2O.SnO^2$, and isomorphous with the corresponding fluosilicates and fluotitanates. (Marignac, Ann. Min. [5], xv. 221; Jahresb. 1859, p. 110.)

The *ammonium-salt*, $2NH^4F.SnF^4$, is obtained by the action of hydrofluoric acid on stannate of ammonium, or, better, by double decomposition of the lead- or silver-salt with sulphate or chloride of ammonium. The crystals, which are seldom distinct, are rhombohedral combinations, united in twins, or complex aggregates.—When evaporated with fluoride of ammonium, it yields the salt $4NH^4F.SnF^4$, in distinct rhombic combinations.

The *barium-salt*, $Ba''F^2.SnF^4$, is obtained, as a sparingly soluble precipitate, by decomposing the zinc-salt with chloride of barium. By slowly cooling a slightly concentrated solution of this precipitate, or by spontaneous evaporation, a hydrate, $Ba''F^2.SnF^4.3H^2O$, is obtained in monoclinic crystalline laminæ, but on evaporating the solution near its boiling-point, the anhydrous salt separates in microscopic indistinct crystals.

The *cadmium-salt*, $Cd''F^2.SnF^4.6H^2O$, is isomorphous with the magnesium-salt.

The *calcium-* and *strontium-salts* form monoclinic crystals containing 2 at. water.

The *cupric salt*, $Cu''F^2.SnF^4.4H^2O$, forms blue monoclinic crystals, permanent in the air.

The *lead-salt*, $PbF^2.SnF^4.3H^2O$, crystallises with difficulty in thin nacreous laminæ, isomorphous with the trihydrated barium-salt. It has a great tendency to form supersaturated solutions, which ultimately solidify in nodular crystalline masses.

By recrystallisation from water the salt is decomposed, with separation of lead-fluoride.

The *lithium-salt*, $2LiF.SnF^4.2H^2O$, rarely forms distinct monoclinic crystals: generally only crystalline crusts, or indistinct microscopic crystals.

The *magnesium-salt*, $Mg''F^2.SnF^4.6H^2O$, crystallises in hexagonal combinations, permanent in the air.—The *manganese-salt*, $Mn''F^2.SnF^4.6H^2O$, forms pale-red shining crystals, isomorphous with the last, and gradually becoming dull on exposure to the air.—The *nickel-salt*, $NiF^2.SnF^4.6H^2O$, is likewise isomorphous with the magnesium-salt.

The *potassium-salt*, $2KF.SnF^4.H^2O$, is obtained by saturating a solution of potassic stannate with hydrofluoric acid, and evaporating, in laminar crystals, which dissolve in 2·3 pts. of boiling water, and in 15 to 16 pts. water at 18°. Sometimes, especially on recrystallising with addition of a drop of hydrofluoric acid, a salt, identical in composition with that just described, is obtained in granular crystals having the form of rhombic pyramids, soluble in 3 pts. boiling water and in 27 pts. water at 18°. The crystals of both kinds retain their water till heated above 100°, and melt at a red heat, with loss of hydrofluoric acid.—An *acid potassium-salt*, $2(2KF.SnF^4).(KF.HF)$, or $2K^2Sn^{iv}F^6.KHF^2$, crystallises in needle-shaped monoclinic combinations.

The *silver-salt*, $2AgF.SnF^4.4H^2O$, forms indistinct crystals, which melt below 100°, but do not give off their water till heated to a higher temperature, at which also hydrofluoric acid is given off.

The *sodium-salt*, $2NaF.SnF^4$, has not been obtained in distinct crystals: it dissolves in 18 to 19 pts. of water at 20°.

The *zinc-salt*, $ZnF^2.SnF^4.6H^2O$, is isomorphous with the magnesium-salt, and easily soluble in water.

TIN, IODIDES OF. There are two iodides of tin analogous to the protoxide and dioxide. The existence of a sesquioxide, Sn^4I^6, is doubtful. A solution of iodine in iodide of potassium (1 at. iodine to 2 at. KI) does not precipitate a solution of stannic chloride, but on evaporation a yellow powder is deposited, which may possibly be the sesqui-iodide. (Boullay.)

Di-iodide of Tin, or *Stannous Iodide.*—This compound is produced:—1. By heating 1 pt. of tin with 2 pts. of iodine till the iodine melts. A violent action then takes place, and a brown mass is formed, consisting of stannous and stannic iodides, the latter of which may be separated by sublimation, while the stannous iodide remains in the form of a red crystalline mass.—2. By adding iodide of potassium in slight excess to a warm concentrated solution of stannous chloride, the liquid, as it cools, depositing stannous iodide in yellowish-red needles.—3. By the action of hydriodic acid on tin or the dichloride. When moderately concentrated hydriodic acid is placed in contact with strips of tinfoil, or with tin-filings, in a long glass tube, and kept in gentle ebullition for several days, or heated in a sealed tube to 120°—150° for some hours, stannous iodide is formed, in shining yellowish-red prisms (Wöhler and Dünhaupt, Ann. Ch. Pharm. lxxxvi. 374). Tin, heated with iodide of amyl to 180°, in a sealed tube for some time, is converted, partly into yellowish-red quadratic octahedrons, partly into sulphur-yellow prisms, which quickly turn red in contact with the air: these compounds have not been analysed.

Stannous iodide, heated in a close vessel, melts to a dark-red crystalline mass, yielding a cinnabar-coloured powder. When heated in contact with the air, it is decomposed, stannic iodide subliming, and stannous oxide remaining. It is slightly soluble in cold, somewhat more soluble in hot water, and is not decomposed thereby. A solution of stannous iodide is likewise formed by heating tin with water and iodine. Stannous iodide dissolves also in aqueous stannous chloride.

Compounds of Stannous Iodide.—*a.* With stannous chloride.—An aqueous solution of stannous chloride mixed with iodine, deposits stannous iodide; and on evaporating the remaining liquid (which contains stannic chloride, stannous chloride, and stannous iodide), stannous chloriodide, SnClI or $SnCl^2.SnI^2$, separates in straw-yellow, non-volatile crystals, which are decomposed by water, with separation of stannous iodide. (Henry.)

β. With stannous oxide.—Stannous iodide is decomposed by a large excess of water, forming hydriodic acid which dissolves, and stannous oxide which unites with the undecomposed iodide, forming, according to Personne (Compt. rend. liv. 216), insoluble oxyiodides of variable composition, which are yellow, pulverulent, and are decomposed by a large quantity of water. Personne analysed four of these compounds, ing $Sn^3IO^2 = SnI^2.2SnO$; $Sn^2I^2O = SnI^2.SnO$; $Sn^3I^4O = 2SnI^2.SnO$; and $3SnI^2.SnO$.

ammonia.—100 pts. stannous iodide absorb 20 pts. ammonia-gas, form- compound, which in the pure state is probably $2NH^3.SnI^2$, or iodide of ium $(N^2H^6Sn'')I^2$. (Rammelsberg, Pogg. Ann. xlviii. 169.)

5. With other metallic iodides.—Stannous iodide unites with the iodides of the alkali-metals and alkaline earth-metals, forming double salts, which may be obtained either by direct mixture of the solutions of the constituent iodides, or by mixing a solution of stannous chloride with excess of a metallic iodide. They must be crystallised from alcohol, as they are decomposed by water, forming stannous oxyiodides, similar to those produced from stannous iodide and water.

The *ammonium-salt*, $2NH^4I.SnI^2$, forms greenish-yellow needles (Boullay). According to Personne, there is also a salt containing $NH^4I.SnI^2.\frac{3}{2}H^2O$.—The *potassium-salt*, $2KI.SnI^2$, forms yellowish silky needles, which, when heated in chlorine gas, yield stannic chloride, chloride of potassium, and free iodine (Boullay). Personne likewise obtained the hydrated salt, $KI.SnI^2.\frac{3}{2}H^2O$.—The *sodium-salt*, $NaI.SnI^2$, forms pale-yellow crystals.

Stannous iodide also forms crystallisable double salts with the iodides of *barium* and *strontium*.

Tetraiodide of Tin, or *Stannic Iodide*, SnI^4, is formed, together with stannous iodide, by heating tin-filings with iodine in a sealed tube, combination taking place with incandescence at 50°. It may be separated from the stannous iodide by its greater volatility. It is also produced by the action of iodine on stannous chloride, or by dissolving stannic hydrate in hydriodic acid. (Berzelius.)

Sublimed stannic iodide forms yellowish-red octahedrons, of specific gravity 4·696. It melts at 146°, solidifies at 142°, sublimes at 180°, and boils at 295°. It is decomposed by water, completely at the boiling heat, into hydriodic acid and stannic hydrate. It dissolves in alcohol, ether, and benzene.

Stannic iodide does not combine either with stannic hydrate, or with the iodides of the alkali-metals. It easily absorbs dry ammonia-gas, forming at first a yellow body, $3NH^3.SnI^4$, and by further assumption of ammonia, the two compounds, $4NH^3.SnI^4$ and $6NH^3.SnI^4$. (Personne.)

TIN, OXIDES OF. Tin forms three oxides: a protoxide, a sesquioxide, and a dioxide.

Protoxide of Tin, or **Stannous Oxide,** SnO.—This oxide is produced: 1. By heating stannous oxalate out of contact with air (Liebig).—2. By precipitating stannous chloride with carbonate of sodium, and heating the washed and dried precipitate of stannous hydrate in an atmosphere of hydrogen or carbonic anhydride, to a temperature not exceeding 80°; the anhydrous oxide is thus obtained as a brown or black powder (Berzelius). According to Otto, the hydrate sometimes changes to the black oxide on the filter, or on the sides of the precipitating vessel, where it is touched with a glass rod.—3. Stannous hydrate, boiled with a quantity of caustic potash or soda less than sufficient to dissolve it, is converted into small, black, shining crystals of the anhydrous oxide (Frémy, Berz. Jahresb. xxiv. 133; xxv. 172).—4. A solution of stannous chloride is evaporated in contact with metallic tin, till a residue of the fused chloride is obtained; this, after removal of the metallic tin, is heated with 1 at. or more of crystallised sodic carbonate till it turns black, and the stannous oxide thus produced is washed and dried. (Sandall, J. pr. Chem. xiv. 254.)

Stannous oxide is a black powder, of specific gravity 6·666 (Berzelius); bluish-black or slate-grey (Sandall). The crystals obtained by the third process are, according to Nordenskjöld, monometric, exhibiting the combination $\infty O \,.\, \infty O \infty$, have a specific gravity of 6·1, and yield a greenish-brown powder. When heated to 258°, they decrepitate, swell up, and are resolved into olive-green laminæ, soft to the touch (Frémy). This olive-green modification is likewise obtained by boiling stannous hydrate with excess of ammonia (Gay-Lussac). A third modification is obtained by evaporating a very dilute solution of sal-ammoniac in which hydrated stannous oxide is diffused, that compound being converted, as soon as the sal-ammoniac crystallises, into anhydrous stannous oxide having the form of a cinnabar-coloured powder (Frémy). The red modification is also produced by digesting thoroughly-washed hydrated stannous oxide, at a temperature of 133°, in a slightly acid solution of stannous acetate having a density of 1·06. The oxide is then obtained in heavy, hard, crystalline grains, which yield a greenish-brown powder by trituration, and blacken when exposed to sunshine. (Roth, Ann. Ch. Pharm. lx. 214.)

Stannous oxide is permanent in the air at ordinary temperatures, but easily oxidises to stannic oxide when heated. When dry, it may be set on fire by a glowing body, and then burns to stannic oxide. It is reduced at a red heat by *hydrogen* or *charcoal*, and when heated before the blowpipe with *carbonate of sodium* (best with addition of cyanide of potassium), it yields a button of metal.—Heated in *chlorine-gas* it is converted into stannic chloride and stannic oxide. When ignited with *sulphur*, it yields stannic sulphide and sulphurous anhydride. By boiling with caustic *potash* or *soda*, it is converted into a stannate of the alkali-metal, with separation of tin.—With *acids*, it forms the stannous salts.

Stannous Hydrate, $Sn^2H^2O^3 = 2SnO.H^2O$, is obtained, as a white precipitate, by decomposing a stannous salt with an alkaline carbonate. It dissolves in acids and in the fixed alkalis much more easily than the anhydrous oxide, but is insoluble in ammonia. When boiled with water or with aqueous alkalis, or when gently heated in the dry state, it is converted into the anhydrous oxide. When exposed to the air, it gradually takes up oxygen, and is converted into stannic hydrate. When boiled with strong potash-ley, it yields stannate of potassium and metallic tin.

Stannous hydrate acts as a deoxidising agent, like the corresponding chloride (p. 806), reducing some metallic oxides to metal, others to a lower state of oxidation. Its action on *cupric oxide* has been specially studied by Lenssen (J. pr. Chem. lxxxix. 90; Jahresb. 1860, p. 182). When a solution of stannous hydrate in alkaline carbonate is mixed with an alkaline cupric solution (prepared with cupric sulphate, tartaric acid, and sodic carbonate), a flesh-coloured precipitate is at first produced, consisting of cuprous and stannous oxides; and on adding more cupric sulphate, a red precipitate is formed, containing cuprous and stannic oxides. When solutions of stannous and cupric oxide in caustic alkali are mixed together, cuprous oxide is precipitated, together with stannic oxide.—With excess of the tin-solution, a yellowish liquid is produced, which, when heated, deposits a black powder, composed of $Cu^2O.3SnO.SnO^2.5H^2O$. This compound acquires a tinge of green in drying, gives off 2 at. water at 100°, and when heated in the air, oxidises with incandescence, and then contains cuprous and stannic oxides.—When a boiling solution of stannous oxide in caustic alkali is mixed with a small quantity of alkaline cupric solution, a heavy black powder is deposited, which acquires metallic lustre by burnishing; this body contains 79·1 per cent. copper to 14·8 tin; therefore 10 at. copper to 1 at. tin and 3 at. oxygen: hence it appears to be an alloy of copper and tin mixed with cuprous or stannous oxide.

Sesquioxide of Tin, Sn^2O^3.—This oxide was obtained by Fuchs, in combination with water, by diffusing recently precipitated ferric oxide in a solution of stannous chloride not containing any excess of acid, and afterwards boiling the mixture. Sesquioxide of tin is then precipitated, and ferrous chloride remains in solution:

$$2SnCl^2 + Fe^2O^3 = Sn^2O^3 + 2FeCl^2.$$

The sesquioxide thus obtained is a slimy grey matter, generally yellow from adhering oxide of iron. Ammonia dissolves it easily and without residue, a character which distinguishes this oxide from the protoxide of tin, the latter being insoluble, or nearly so, in ammonia. Sesquioxide of tin is dissolved by concentrated hydrochloric acid; the taste of the solution is not metallic. The solution is distinguished from that of a stannic salt, by producing the characteristic purple precipitate with chloride of gold. Sesquioxide of tin does not appear to form definite salts.

Dioxide of Tin, or **Stannic Oxide,** SnO^2.—This oxide occurs native as *Tinstone* or *Cassiterite*, being in fact the principal ore of tin (p. 798). It forms quadratic crystals, usually exhibiting the combination $P . \infty P . P\infty . \infty P\infty$ (*fig.* 322, vol. ii. p. 160). The prismatic faces are often but little developed, and $P\infty$ is often absent altogether. The combinations $P . \infty P . \infty P\frac{3}{2}$, and $P . \infty P . 3P\frac{3}{2}$, likewise occur. For P, the length of the principal axis is 0·6743. Angle P : P (terminal) = 121° 35′; P : P (lateral) = 87° 17′. Twins occur like *fig.* 323. The crystals cleave imperfectly parallel to ∞P and $\infty P\infty$, and in traces parallel to P. The mineral occurs also in imbedded and implanted crystals, and in botryoïdal or reniform shapes, with fibrous divergent structure, and composed of concentric coats, constituting the variety called *wood-tin*, or, when it occurs in small lumps, *toad's-eye-tin*; also massive, granular or impalpable. Hardness = 6 to 7. Specific gravity = 6·3 to 7·1. Lustre adamantine; crystals usually splendent. Colour brown or black, sometimes red grey, or yellow; rarely colourless. Streak white, greyish, or brownish. Nearly transparent—translucent. Fracture subconchoïdal, uneven. Brittle.

Analyses.—*a.* From Schlackenwald, in Bohemia (Klaproth, *Beiträge*, ii. 245).—*b.* Alternon, in Cornwall (Klaproth).—*c.* Finbo, near Fahlun, in Sweden (Berzelius, Schw. J. xvi. 256).—*d.* County of Wicklow, Ireland: brown grains from the sand: specific gravity = 6·753 (Mallet, Dublin Geol. Soc. J. iv. 272).—*e.* Xeres, in Mexico: dark-brown wood-tin, yielding a red powder: specific gravity = 6·862 (Bergemann, Leonh. Jahresb. 1857, p. 395).—*f*, *g*. From the sand of the Tipuani river in Bolivia, occurring with gold, metallic tin, and several other minerals: *f.* brownish, *g.* black; specific gravity = 7·021 (D. Forbes, Phil. Mag. [4], xxx. 139):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
Stannic oxide	95·4	98·60	93·6	95·26	89·43	91·81	91·80
Tantalic oxide	. .	. .	2·4				
Silica	. .	0·75	. .	0·84	2·21		
Ferric oxide	0·7	0·36	1·4	2·41	6·63	1·02	2·69
Manganic oxide	. .	. .	0·8	. .	. .		
Alumina	. .	. .	. .	. .	1·20	0·73	
Insoluble matter	. .	. .	. .	. .	. .	6·48	5·51
	96·1	99·71	98·2	98·51	99·47	100·04	100·00

A colourless specimen from the last-mentioned locality, of specific gravity 6·843 (also after strong ignition), was found by Forbes to consist of nearly pure stannic oxide. A specimen from Carabuco, in Bolivia, occurring in prisms of specific gravity 6·4, was found by Kröber to contain 96·339 per cent. stannic oxide, 2·177 ferric oxide, 0·0115 silver, 0·20 tungstic anhydride, 0·250 lead, and 1·737 water (= 100·538). Chandler (Sill. Am. J. [2], xxxix. 340) found in a tinstone from Durango, in Mexico, about 95·9 per cent. stannic oxide, and 4·1 topaz, in crystals of various size.

Stannic oxide may be crystallised artificially:—1. By passing the vapour of stannic chloride mixed with aqueous vapour through an ignited porcelain tube; larger crystals are, however, obtained by diffusing the vapour of the stannic chloride through a stream of dry carbonic anhydride, instead of volatilising it by heat, and then passing it, mixed with steam, through the ignited tube. The crystals thus obtained are colourless, with an adamantine lustre, and a specific gravity of 6·72, and are hard enough to scratch glass: they are trimetric prisms, isomorphous with the variety of native titanic oxide called brookite, and therefore different from those of native tinstone, which are quadratic, and isomorphous with anatase. Stannic oxide is therefore dimorphous (Daubrée, Pharm. Centr. 1849, p. 821).—2. By igniting amorphous stannic oxide in a stream of hydrochloric acid gas, the crystals being larger with a rapid than with a slow current of the gas. These crystals are quadratic, like those of native tinstone (Deville, Compt. rend. liii. 161).—3. The formation of crystallised stannic oxide has been observed to take place in fusing the dross or slag collected on the hearth of a furnace used for casting gun-metal. The crystals thus produced were very hard, brittle, four-sided prisms, similar in form to those obtained by Daubrée. (Abel, Chem. Soc. Qu. J. x. 119.)

Amorphous stannic oxide is easily obtained by heating tin in contact with the air. A grey film is first formed, consisting of a mixture of stannic oxide and metallic tin, formerly called *Civis jovialis* (a name afterwards applied to stannic oxide itself); by further heating, it is converted into pure stannic oxide. Tin, when rapidly heated to its boiling-point, burns with a white flame, yielding flocks of stannic oxide, formerly called *Flores stanni*, s. *Fl. Jovis*. Stannic oxide is also formed by igniting the protoxide or sesquioxide, or the corresponding hydrates, in contact with the air. Stannous oxalate, heated in small quantities in contact with the air, yields very hard stannic oxide. (Vogel, Pharm. Centr. 1855, p. 413.)

Amorphous stannic oxide is a white or yellowish powder, assuming, when heated, a transient dark-yellow or brown colour. Its specific gravity is 6·6 to 6·9; its cubical expansion, between 0° and 100°, is 0·0016 (Kopp), 0·0017 (Joule and Playfair). It is hard, and is therefore used for polishing stone and glass, and for sharpening and polishing steel, &c. The oxide used for this purpose is called **putty-powder**; it is sometimes a mixture of the oxides of tin and lead.

Stannic oxide, whether crystallised or amorphous, is very difficult to fuse, and not at all volatile. It is not attacked by acids, even in the concentrated state. According to Rose, it forms, when heated with the strongest *sulphuric acid*, a syrupy liquid, which deposits the whole of the stannic oxide on dilution with water. When fused with *acid sulphate of potassium*, it dissolves, but separates completely from the fused mass on addition of water. It is not dissolved by fusion with alkaline carbonates, but is rendered soluble by fusion with *caustic alkali*. When fused with *sulphur*, it yields sulphide of tin and sulphurous anhydride; by ignition in *chlorine-gas*, it is converted into stannic chloride; even natural tinstone is decomposed in this manner. It is reduced to the metallic state by ignition with *hydrogen*, *charcoal*, *carbonic oxide*, and *carburetted hydrogen-gas*; also by heating with *potassium* and *sodium*.

Stannic oxide is much used in the preparation of enamel, to render the glass opaque, and in the manufacture of opaque glasses in general.

Stannic Hydrates and Salts.

Stannic oxide forms two hydrates, differing from one another in composition and properties—both however being acids, and capable of forming salts by exchanging their hydrogen for metals. These hydrates or acids are **stannic acid**, $SnO^2.H^2O$ =

$H^2Sn^{iv}O^3$, and **metastannic acid**, $Sn^5O^{10}.5H^2O = H^{10}Sn^5O^{15}$, the former being capable of exchanging the whole of its hydrogen for metal, and forming the stannates which contain M^2SnO^3, whereas the latter exchanges only one-fifth of its hydrogen for metals, forming the metastannates, $M^2H^8Sn^5O^{15}$. Berzelius, who first observed the differences between these two acids, supposed them to contain different modifications of stannic oxide; but the polymerism of the two hydrates, and the diversities of composition of their corresponding salts, is quite sufficient to account for their differences of character without the aid of any such hypothesis (Frémy, Ann. Ch Phys. [3], xii. 462; xxiii. 393). According to R. Weber, however (Pogg. Ann. cxxii. 358; Jahresb. 1864, p. 243), stannic and metastannic acids exhibit no essential differences in their behaviour towards bases. He finds, indeed, that normal stannate of potassium can take up a large quantity of stannic hydrate, forming a clear solution, which, when evaporated over oil of vitriol, leaves a hydrated salt containing 1 at. K^2O to 5 at. SnO^2; and that metastannic acid dissolved to saturation in potash-ley, and evaporated in like manner, yields a salt containing 1 at. K^2O to 6 or 7 at. SnO^2. Hence Weber concludes that the relations of stannic and metastannic acids to bases are not essentially different, and that their supposed polymerism has no existence; but his results require confirmation.

STANNIC ACID.—This hydrate is precipitated by acids from solutions of alkaline stannates, also from the solution of stannic chloride by a carbonate of barium or calcium, not in excess; alkaline carbonates throw down an acid stannate. When dried in a vacuum, it has the composition $SnO^2.H^2O = SnH^2O^3$; after drying in a stream of dry air, it contains 22·5 per cent. water, corresponding with the formula $3SnO^2.7H^2O$, or $3SnH^2O^3.4H^2O$; and at 140° it gives off 5 at. water, leaving the hydrate $3SnO^2.2H^2O$, which has the same composition as metastannic acid dried at the same temperature (p. 820).

Stannic acid, when recently precipitated, is gelatinous; after drying in the air, it forms hard translucent lumps, like gum-arabic, which redden litmus. According to Weber, stannic acid dried in the air at ordinary temperatures contains $SnO^2.2H^2O$, and has therefore the same percentage composition as air-dried metastannic acid.

Stannic hydrate dissolves in the stronger acids, forming the **stannic salts**. These salts are also formed by exposing solutions of stannous salts containing excess of acid to the air, or by treating them with chlorine, or with a small quantity of nitric acid. The solution of stannic hydrate in hydrochloric acid is identical with aqueous stannic chloride. The stannic salts of oxygen-acids are very unstable. The general reactions of the stannic salts have been already described (p. 810). The individual salts are described under the respective acids.

Stannates.—Stannic hydrate exhibits acid much more decidedly than basic properties. It forms easily soluble salts with the alkali-metals, and from these the insoluble stannates of the earth-metals and heavy metals are obtained by double decomposition. The stannates are decomposed by acids, yielding gelatinous stannic acid. The general formula of the normal stannates is $M^2Sn^{iv}O^3 = M^2O.SnO^2$. They have been examined chiefly by Frémy (*loc. cit.*) and Moberg. (J. pr. Chem. xxviii. 230.)

Stannate of Ammonium.—An acid salt, $(NH^4)^2SnO^3.SnO^2.xH^2O$, remains as a yellowish jelly on evaporating an ammoniacal solution of stannic acid over oil of vitriol (Moberg). A stannate of ammonium is also precipitated, on mixing a solution of potassic stannate with sal-ammoniac, as a gelatinous mass, which dissolves in pure water, but is reprecipitated by ammonia. (Berzelius.)

Stannate of Potassium, $K^2SnO^3 = K^2O.SnO^2$, is prepared by dissolving stannic acid in potash-ley, or by fusing metastannic acid or anhydrous stannic oxide with hydrate of potassium, till a sample mixed with nitric acid gives a precipitate which redissolves in excess of nitric acid. The solution, evaporated over oil of vitriol, yields transparent rhombic prisms, containing $K^2SnO^3.4H^2O$, according to Frémy; $K^2SnO^3.3H^2O$, according to Moberg (*loc. cit.*), Marignac (Ann. Min. [3], xv. 277), and Ordway (Sill. Am. J. [2], xl. 473). Marignac prepares the salt by gradually adding 30 pts. metastannic acid to 80 pts. fused hydrate of potassium till the mixture boils up. The mass, if it has not been too strongly heated, dissolves almost wholly in water; and on evaporating the liquid, the salt is obtained in crystals, which are rhombohedral combinations, often forming twins, and always with curved faces.

Ordway prepares pure stannate of potassium by mixing the solution of the crude commercial salt (obtained by igniting tin with hydrate and nitrate of potassium) with an equal volume of strong alcohol, repeatedly treating the syrupy layer which separates, with alcohol, pressing the pasty mass ultimately obtained (which still contains free alkali), then dissolving it in water, and washing with alcohol. The concentrated solution [illegible] in a vacuum yields the salt in hard, transparent, monoclinic crystals, of [illegible] 3·197.

Stannate of potassium gives off its water at a red heat. It has an alkaline reaction, dissolves easily in water, but is insoluble in alcohol. According to Ordway, 100 pts. water, at 10°, dissolve 106·6 pts. of the salt, forming a solution of specific gravity 1·618; and at 20°, the same quantity of water dissolves 110·5 pts. of the salt, forming a solution of specific gravity 1·627. The aqueous solution is precipitated by chloride of ammonium, but not by chloride of potassium or sodium. Dilute acids do not form a permanent precipitate till three-fourths of the alkali are neutralised. A solution, neutralised up to this point, yields, with alcohol, a white flocculent precipitate of potassic metastannate. (Ordway.)

Stannate of potassium is used in calico-printing for the same purposes as stannate of sodium, and is prepared, on the large scale, by similar processes (*infra*).

Stannate of Sodium, $Na^2SnO^3 = Na^2O.SnO^2$, is formed in the same manner as the potassium-salt, and separates from the alkaline liquid, on heating, in the crystalline form; by solution in water, it is obtained in fine hexagonal plates, containing $Na^2SnO^3.3H^2O$ (Moberg; Rammelsberg; Ordway). Marignac, by proceeding in the same way as for the preparation of the potassium-salt, obtains stannate of sodium in rhombohedral crystals, with curved faces. Ordway obtains pure stannate of sodium as a crystalline precipitate, by adding acetate of barium to the aqueous solution of the commercial salt, and mixing the filtered liquid with about an equal volume of alcohol. If only so much alcohol be added as not to produce permanent turbidity, the salt separates in transparent crystals. H. Jonas (Chem. Centr. 1865, p. 607), by recrystallising the commercial salt, obtained pure sodic stannate, in oblique rhombic prisms containing $Na^2SnO^3.9H^2O$.

Stannate of sodium is less soluble in warm than in cold water, and consequently separates on heating a solution prepared in the cold. According to Ordway, 100 pts. water dissolve 67·4 pts. of it at 0°, and 61·3 pts. at 20°. According to Haeffely (Dingl. pol. J. cxliv. 66), a solution of sodic stannate, of specific gravity 1·3, deposits, when heated, crystals of the composition above given; on cooling, however, these crystals redissolve, so that the solution acquires a specific gravity of 1·35; it then gradually deposits crystals containing $Na^2SnO^3.8H^2O$, the aqueous solution of which yields immediately when heated, and in the course of some weeks at ordinary temperatures, crystalline metastannate of sodium.

A solution of stannate of sodium is used in calico-printing as a "preparing salt," or mordant, chiefly for fabrics composed of wool and cotton together; it serves to render the cotton-fibre more susceptible of taking the dye, so that the whole fabric, when taken out of the dye-bath, or the steam-chamber, may exhibit a uniform depth of colour. The dilute solution, when brought in contact with the fibre, deposits stannic hydrate upon it, which binds the colouring-matter, the action being assisted by boiling, by the influence of atmospheric carbonic acid, or by the addition of a little sulphuric acid or sal-ammoniac to the bath.

Stannate of sodium is prepared, on the large scale, for these purposes by fusing tinstone with hydrate, nitrate, chloride, or sulphide of sodium; by boiling the tin-ore with caustic soda-ley; by fusing metallic tin with a mixture of carbonate and nitrate of sodium, or heating it with soda-ley mixed with nitrate and chloride of sodium, and evaporating the solution in an iron pot till it becomes heated to the melting-point of tin. Haeffely prepares it by heating soda-ley with tin and litharge; stannate of sodium is then formed, and metallic lead separated in the form of a sponge, which quickly reoxidises when heated in contact with the air. In this process, tin containing lead, or the cuttings of tinplate (tinned iron), may be used instead of pure tin. [For details of the several manufacturing processes, see Richardson and Watts's *Chemical Technology*, vol. i. pt. iv. p. 35, and pt. v. p. 342.]

An *arsenio-stannate of sodium*, $Na^2O.6SnO^2.2As^2O^5 + 5aq.$, is sometimes used in English dyehouses and printworks. It is prepared by adding nitric acid in excess to a boiling solution of stannate and arsenate of sodium containing an excess of the latter, and treating the resulting gelatinous precipitate, $2SnO^2.As^2O^5.10H^2O$, with excess of soda. The arsenio-stannate then separates in shining needles, while ordinary stannate of sodium remains in solution. This arsenical salt is said to be more economical in use than the ordinary stannate; but it does not produce brighter colours than the latter, and is likely to be prejudicial to the health of the workmen. (Haeffely, Dingl. pol. J. cxl. 290.)

The *stannates of barium, calcium*, and *strontium* may be prepared by boiling a solution of the potassium- or sodium-salt with the hydrates or carbonates of the alkaline earth-metals, or by calcining a mixture of tin-ore with lime, baryta, or strontia, or with the corresponding nitrates at a high degree of heat in a reverberatory furnace. These earthy stannates, when decomposed by hydrochloric acid, yield pure stannic acid, which may be used for the preparation of the alkaline stannates. (James Young's patent, 1848, No. 12,359, and 1849, No. 12,744.)

Stannates of Copper.—The *cupric salt*, which is used as a non-arsenical green pigment, may be prepared by adding a solution of 1 at. tin (118 pts.) in nitromuriatic acid, to a solution of 1 at. cupric sulphate (250 pts.), then adding caustic soda in excess, and washing and drying the resulting precipitate; or by igniting 100 pts. nitrate of sodium with 59 pts. tin, dissolving the mass in water, and using the solution to precipitate cupric sulphate (Gentele).—The *cuprous salt*, which has not yet been obtained pure, is formed, together with other products, in the action of stannous hydrate on cupric oxide, both in alkaline solution (p. 816).

Metastannic Acid, $Sn^5H^{10}O^{15} = Sn^5O^{10}.5H^2O$.—Produced by the action of nitric acid upon tin. Tin treated with strong nitric acid is completely transformed into a white powder, which, when dried in the air at ordinary temperatures, contains $Sn^5O^{10}.10H^2O = Sn^5H^{10}O^{15}.5H^2O$, or $5SnO^2.10H^2O$; but when heated for some time to 100°, it gives off 5 at. water, and is reduced to $Sn^5H^{10}O^{15}$, or $5SnO^2.5H^2O$. At 140° it gives off more water, leaving the hydrate $3SnO^2.2H^2O$ (or $5SnO^2.4H^2O$, according to Frémy's later statements); at 160° it is converted into $5SnO^2.3H^2O$, and at a red heat, into anhydrous stannic oxide.

According to Weber, nitric acid of specific gravity 1·2 converts tin, at ordinary temperatures, into stannous nitrate, stannic acid, and metastannic acid, which is coloured yellow by admixed stannous metastannate. With nitric acid of specific gravity 1·35, the products, if the liquid is well cooled, are metastannic acid [? stannic] and stannic nitrate; by dilution and heating, the stannic acid is converted into insoluble metastannic acid, which indeed is always produced under the influence of heat.

Metastannic acid is white, crystalline, insoluble in water, and in nitric acid. It takes up hydrochloric or sulphuric acid without dissolving in it.

The sulphuric compound is decomposed by water, which removes the whole of the sulphuric acid. The compound with hydrochloric acid dissolves in pure water, but is precipitated from the solution by strong hydrochloric acid. On distilling the solution, hydrochloric acid is given off, with only traces of stannic chloride, and metastannic acid remains. According to Weber, the solution, evaporated over oil of vitriol, leaves a residue consisting of $SnCl^4.3SnO^2.5H^2O$. The same solution becomes turbid on boiling, and by prolonged ebullition with fresh quantities of water, the whole of the metastannic acid is separated, the more quickly as the solution is more dilute (Frémy). (For the reactions of the hydrochloric acid solutions with acids, alkalis, &c., see p. 811). A dilute solution of ordinary stannic acid in hydrochloric acid undergoes a gradual change, and, after some time, exhibits the characters of a solution of metastannic acid. The transformation is quicker as the solution is more dilute, and in very concentrated solutions it does not take place at all; in a dilute solution also, the change may be prevented by addition of tartaric acid. The gradual transformation of stannic into metastannic acid may be recognised by the reaction of the solution with sulphuric acid, stannous chloride, ammonia, tartaric acid, and ferrocyanide of potassium (p. 811).

On the other hand, metastannic acid is converted into normal stannic chloride by prolonged digestion with strong hydrochloric acid, especially at the boiling heat. When heated in dry hydrochloric acid gas, it yields a distillate of stannic chloride, from which ordinary stannic acid may be obtained. By fusion with excess of a caustic alkali, metastannic acid is completely converted into ordinary stannic acid.

Metastannates.—These salts may for the most part be represented by the formula $M^2H^8Sn^5O^{15}$, or $M^2O.4H^2O.5SnO^2$. They exist only in the hydrated state, being decomposed when deprived of their basic water. Löwenthal supposes that pure metastannic acid does not unite directly with alkalis, but that the so-called metastannates are mixtures of ordinary stannates with metastannic acid, the quantity of this acid contained in them being less in proportion as the acid used in their preparation had been more completely converted into ordinary stannic acid: hence the variations which have been observed in the composition of some of these salts.

Metastannic acid dissolves slowly in alkalis, and is gradually deposited in its original state, as the solution absorbs carbonic acid from the air. From solutions of the alkaline metastannates, acids throw down metastannic acid, insoluble in nitric acid, but soluble in ammonia, whereas the original metastannic acid formed by the action of nitric acid upon tin is insoluble in ammonia.

The metastannates of potassium and sodium, heated with excess of base, are transformed into stannates. They are soluble in water. The other metastannates are insoluble, and are obtained by double decomposition.

Metastannate of Potassium, $K^2H^8Sn^5O^{15}$, is prepared by dissolving metastannic acid in cold potash; it may be precipitated in the solid state by adding pieces of potash to the liquid. It is gummy, uncrystallisable, and strongly alkaline. At a red heat, it gives off its water, and is decomposed; the calcined mass, digested in water, yields up all its alkali, and leaves nearly pure stannic oxide (Frémy).—Another metastannate of potassium, containing, according to Weber, $K^2H^6Sn^7O^{18}$ or $K^2O.3H^2O.7SnO^2$, was prepared by Rose, by adding caustic potash-ley to the solution of metastannic acid in hydrochloric acid, till the precipitate at first formed was redissolved, and then precipitating with alcohol. This salt is soluble in water; the solution, when heated, does not become turbid, but gelatinises after a while; it is precipitated by potash and by many salts, and leaves a gummy residue when evaporated.

Metastannate of Sodium, $Na^2H^8Sn^5O^{15}$, is obtained like the potassium-salt, is white, crystallo-granular, and dissolves slowly but completely in water. The aqueous solution decomposes when gently heated, and on boiling, deposits the whole of the metastannic acid (Frémy). Haeffely describes another sodium-salt, $Na^2H^8Sn^5O^{15}.4H^2O$, which was deposited from a solution of the ordinary stannates, slowly at ordinary temperatures, more quickly when heated.

Stannous Metastannate, $(Sn''H^8)\overset{iv}{Sn^5}O^{15} = SnO.5SnO^2.4H^2O$.—Frémy formerly assigned to this compound the formula $SnO.3H^2O.3SnO^2$; according to Schiff (Ann. Ch. Pharm. cxx. 47), it is $SnO.6SnO^2.4H^2O$; according to Tschermak (Chem. Centr. 1862, p. 305), $SnO.6SnO.9H^2O$. It is formed by placing metastannic acid in contact with stannous chloride. It is yellow, and insoluble in water; at 140° it gives off water, and becomes brown-black, or, if dried in a stream of carbonic anhydride, cinnamon-brown (Schiff); dark-brown (Tschermak). When treated with nitric acid, or heated in contact with the air, it takes up oxygen, and is converted into metastannic acid. It dissolves in potash, and the solution, when boiled, deposits tin like other stannous salts. Hydrochloric acid dissolves it, forming a solution of stannous chloride and hydrochlorate of metastannic acid.

When a solution of hydrochlorate of metastannic acid is mixed with dissolved stannous chloride, a yellowish precipitate is formed, perhaps identical with the body just described. A similar yellow body, containing, according to Schiff, $(Sn''H^{10})\overset{iv}{Sn^6}O^{18}$ or $SnO.6SnO^2.5H^2O$, is formed by the action of stannous chloride on ordinary stannic acid.

When stannic oxide is heated in an atmosphere of carbonic anhydride or ammonia, a brown oxide is formed, containing Sn^8O^{15}, either $SnO.7SnO^2$ or $Sn^2O^3.6SnO^2$. (Tschermak.)

Stannous chloride does not act upon normal stannic chloride; but with anhydrous stannic oxide it forms a chocolate-brown powder, containing $Sn^{21}O^{41}$ or $SnO.20SnO^2$. This substance does not turn yellow when boiled with water; it is less easily attacked by acids than the hydrated yellow compound; but when fused with alkalis it is easily converted into alkaline stannate.

TIN, OXYCHLORIDE OF. See p. 807.

TIN, OXYFLUORIDE OF. See p. 813.

TIN, OXYIODIDE OF. See p. 814.

TIN, PHOSPHIDE OF.—*a*. Formed by throwing phosphorus upon melted tin, or by fusing together equal parts of tin and glacial phosphoric acid, whereby stannic or stannous phosphate is likewise formed (Pelletier, Landgrebe, Schw. J. lv. 106). The compound may also be formed by heating in a blast-furnace for an hour, 6 pts. of tin-filings or 8 of stannic oxide with 1 charcoal, 10 bone-ash, 5 pounded quartz, and 5 boracic acid (Berthier, Ann. Ch. Phys. [2] xxxiii. 180). It is silver-white (lead-coloured, according to Berthier); it may be cut with the knife; extends under the hammer, but at the same time splits into laminæ. Contains from 13 to 14 per cent. of phosphorus, which burns away on the application of heat (Pelletier).—*β*. When the compound of stannic chloride with phosphoretted hydrogen is decomposed by water, the phosphoretted hydrogen, as it escapes, reduces the stannic chloride to the state of stannous chloride, and at the same time precipitates phosphide of tin in the form of a yellow powder, which remains for a long time suspended in the liquid, and oxidises readily in the air. When washed and dried out of contact of air, it exhibits the phosphorus-flame before the blowpipe. When ignited in hydrogen-gas, it gives up its phosphorus, amounting to 55·43—56·88 per cent., and is converted into metallic tin. (H. Rose, Pogg. Ann. xxiv. 326.)

TIN, SELENIDES OF. The *protoselenide*, SnSe, is produced, with incandescence, when tin is heated with selenium (Berzelius); according to Uelsmann (Ann. Ch. Pharm. cxvi. 124), it is also formed even when tin is heated with excess of selenium. It is light-grey with metallic lustre, coarsely laminar with crystalline fracture, and easily cleavable. It does not melt in a glass tube, or decompose when heated in hydrogen-gas; but when heated in contact with the air, it burns without melting, giving off selenium, and forming stannic oxide. The protoselenide is also formed, when selenhydric acid gas is passed into protochloride of tin, as a dark-brown precipitate, which dries up to a nearly black powder, soluble in caustic alkalis and in sulphides of alkali-metals.

The *diselenide*, or *Stannic selenide*, $SnSe^2$, is formed by precipitating aqueous stannic chloride with selenhydric acid. It is a glittering, dark, yellowish-red precipitate, becoming light red-brown when dry. When heated in hydrogen-gas, it gives off half its selenium; it dissolves in caustic alkalis and alkaline sulphides, the solution quickly depositing sulphur when exposed to the air.

According to Little (Ann. Ch. Pharm. cxii. 213), stannic selenide is also formed by heating tin in selenium-vapour, and is then a tin-white, metallically lustrous mass, having a conchoïdal fracture, and a density of 5·133: it is easily fusible, is not attacked by hydrochloric acid, but is easily decomposed by nitric acid; dissolved by nitromuriatic acid.

TIN, SULPHIDES OF. There are three sulphides of tin corresponding to the oxides; the sesquisulphide, however, is perhaps a compound of the other two.

The *protosulphide*, or *Stannous sulphide*, SnS, is formed, with vivid incandescence, when finely-divided tin, such as tinfoil, is heated with sulphur. The resulting mass generally contains metallic tin, and must therefore be pulverised, and repeatedly heated with sulphur in a close vessel. Stannous sulphide thus prepared is a dark, lead-grey, lamino-crystalline mass, of specific gravity 4·8 (Karsten); 5·2 (Boullay), somewhat tough, difficult to pulverise, and less fusible than tin. Becquerel has obtained it by electrolytic action, in white metallically lustrous cubes.

The same compound is obtained, as a brown-black amorphous precipitate, by passing sulphydric acid gas into the solution of a stannous salt. This amorphous sulphide may, however, be rendered crystalline by adding it by small portions, after washing and drying, to anhydrous stannous chloride in the melted state, as long as it is taken up thereby; then leaving the dark-brown liquid to cool, dissolving out the stannous chloride by dilute hydrochloric acid, and removing an admixed dark-brown powder by levigation; stannous sulphide then remains in small, thin, lead-grey, metallically lustrous laminæ, greasy to the touch, and having a specific gravity of 4·973. (Schneider, Pogg. Ann. xcv. 169.)

Stannous sulphide dissolves in boiling *hydrochloric acid*, giving off sulphydric acid, and yielding a solution of stannous chloride. It dissolves but slightly in *monosulphide of ammonium*, even when freshly precipitated, but easily in solutions of *alkaline polysulphides*, or of the monosulphides mixed with sulphur, the protosulphide of tin in either case being converted into disulphide. It is slowly oxidised by heating with *nitric acid*.—*Chlorine-gas*, at ordinary temperatures, converts it into liquid stannic chloride, and a crystalline compound of that substance with tetrachloride of sulphur (H. Rose):

$$2SnS + 8Cl^2 = SnCl^4 + SnCl^4.2SCl^4.$$

When heated in *hydrogen-gas*, it is slowly reduced to the metallic state.—By fusion with *cyanide of potassium*, it yields sulphocyanate of potassium and metallic tin.

Sesquisulphide of Tin, Sn^2S^3, is produced by gently igniting an intimate mixture of 3 pts. stannous sulphide and 1 pt. sulphur in a retort. 100 pts. of stannous sulphide thus treated, take up 10·5 pts. of sulphur. It is greyish-yellow, with metallic lustre. When strongly ignited in a close vessel, it gives off one-third of its sulphur. —With *potash-ley* it yields a solution of potassic stannate and sulphostannate, and a residue of stannous sulphide. Concentrated *hydrochloric acid* converts it into disulphide of tin, leaving half the tin in the form of protoxide. The same compound separates, in the form of a liver-coloured powder, on digesting a saturated solution of a sulphostannate with disulphide of tin. By digestion with caustic potash, it is converted into the black protosulphide. (Berzelius.)

Disulphide of Tin, or *Stannic Sulphide*, SnS^2. *Sulphostannic acid*.—This compound may be produced either in the dry or in the wet way. It cannot, however, be obtained by simply heating tin with sulphur, because the union of tin and sulphur is always attended with great development of heat, sufficient to resolve the disulphide, if formed, into protosulphide and free sulphur. This decomposition may, however, be prevented by adding to the mixture certain volatile substances, such as mercury or sal-ammoniac, which, in passing into vapour, will render latent a certain portion of the heat evolved, and thus keep down the temperature. According to L. Gmelin, however, sal-ammoniac, when present, takes a direct part in the reaction, which then consists of two stages; first, the formation of ammonio-stannous chloride, with evolution of hydrogen and ammonia:

$$Sn + 4NH^4Cl = 2NH^4Cl.SnCl^2 + H^2 + 2NH^3;$$

and, secondly, the formation of stannic sulphide and ammonio-stannic chloride, by the action of the sulphur on the ammonio-stannous chloride:

$$2(2NH^4Cl.SnCl^2) + S^2 = SnS^2 + 2NH^4Cl.SnCl^4 + 2NH^4Cl.$$

The following are some of the mixtures used:

a. Protochloride of tin and sulphur (Proust).—*b*. Equal parts of sifted tin-filings, sulphur, and sal-ammoniac (Pelletier).—*c*. 4 pts. of tin-filings, 3 pts. sulphur, 2 pts. sal-ammoniac (Woulfe).—*d*. A pulverised amalgam of 2 pts. tin and 2 pts. mercury, with 1⅓ pt. sulphur and 1 pt. sal-ammoniac (Thénard).—*e*. A pulverised amalgam of 12 pts. tin and 6 pts. mercury, with 7 pts. sulphur and 6 pts. sal-ammoniac (whereby 1⅓ pt. of volatile liver of sulphur, 13¼ pts. sublimed matter, and 16 pts. of fine, and for the most part sublimed, mosaic gold are obtained) (Woulfe).—*f*. A pulverised amalgam of 12 pts. tin and 3 pts. mercury, with 7 pts. sulphur and 3 pts. sal-ammoniac.—*g*. 2 pts. stannous oxide and 1 pt. sulphur.—*h*. 8 pts stannic oxide, 7 pts. sulphur, and 4 pts. sal-ammoniac (Woulfe).—*i*. 10 pts. stannous sulphide, 5 pts. sulphur, and 4 pts. sal-ammoniac (Woulfe).—*k*. 5 pts. stannous sulphide, 1 pt. stannous chloride, and 2 pts. sulphur.—*l*. 5 pts. stannous sulphide and 8 pts. mercuric chloride; this mixture yields a very beautiful preparation. (Woulfe.)

Either of these mixtures is slowly heated to redness in a glass retort or a loosely covered flask, immersed in a sand-bath. Vapours of mercury, sal-ammoniac, &c. are then given off, afterwards the excess of sulphur; while the stannic sulphide partly remains at the bottom of the vessel, and partly collects in the upper portion, as a sublimate consisting of soft golden-yellow or brownish-yellow laminæ, unctuous to the touch, having a metallic lustre, and a specific gravity of 4·60, according to Karsten—4·4, according to Boullay. This crystalline stannic sulphide is commonly called mosaic gold, *Aurum mosaicum*, s. *musivum*, and as such was known to the alchemists. Stannic sulphide is likewise obtained in gold-coloured spangles, by passing the mixed vapours of stannic chloride and hydric sulphide through a porcelain tube heated to dull redness.

Mosaic gold is sometimes used, in place of the amalgam of tin and zinc, for coating the rubbers of electrical machines; it produces powerful excitation, requires no grease, and does not stick to the glass.

Stannic sulphide is obtained in the amorphous state by passing sulphydric acid into a solution of stannic chloride, or of a stannic salt acidulated with hydrochloric acid. The resulting light-yellow precipitate, after drying, is yellowish-brown and somewhat translucent, still contains a certain quantity of water, and decrepitates when heated.

Stannic sulphide, ignited in a close vessel, is resolved into sulphur and stannous sulphide, a portion, however, subliming without decomposition; in contact with the air, it yields sulphurous anhydride and stannic oxide. In *chlorine-gas* it deliquesces even at ordinary temperatures, forming a brown liquid, which afterwards solidifies to yellow crystals of the compound $SnCl^4.2SCl^4$ (p. 808). Heated with *iodine* in a stream of carbonic anhydride, it yields the compound $SnSI^2.SI^2$, as a brown, crystalline, fusible mass, or a dark-yellow sublimate. This iodosulphide dissolves without decomposition in chloroform and in carbonic disulphide, and separates from the latter solution in rhombic crystals of the colour of potassic dichromate. It is decomposed by water into sulphur, stannic sulphide, and hydriodic acid, similarly by aqueous alkalis; *alcohol* decomposes it, with separation of sulphur; *hydrochloric* and *nitric acids* separate sulphur from it. (Schneider, J. pr. Chem. lxxix. 419.)

A boiling alcoholic solution of *iodine* does not attack crystalline mosaic gold, but slowly dissolves amorphous stannic sulphide; and the solution yields crystals identical with those of the compound $SnSI^2.SI^2$, deposited from solution in carbonic disulphide. (Schneider.)

Crystalline stannic sulphide is not decomposed by *hydrochloric acid*; the amorphous sulphide boiled with concentrated hydrochloric acid is slowly dissolved, with evolution of sulphydric acid. Hot *nitric acid* oxidises only the amorphous sulphide: boiling *nitromuriatic acid* likewise oxidises mosaic gold, forming sulphuric acid and stannic oxide. Stannic sulphide fused with *litharge* yields, either by partial mutual decomposition, a mixture of the sulphides and oxides of tin and lead; or, if the litharge is in excess, it yields metallic lead, sulphurous anhydride, and a yellow glass.

Sulphostannates.—Stannic sulphide reacts as a sulphur-acid or sulphanhydride, forming sulphur-salts with the more basic metallic sulphides. The sulphostannates of the alkali-metals are produced by fusing tin with the polysulphides of the alkali-metals, or by dissolving stannic sulphide in the aqueous sulphides or hydrates of the same metals; in the latter case, an oxygen-salt is produced simultaneously with the sulphur-salt.

The sulphostannates of the alkali-metals are soluble in water; those of all other metals are insoluble, and are obtained by precipitation, the precipitates being sometimes yellowish, but mostly brown or black. (Kühn, Ann. Ch. Pharm. lxxxiv. 110.)

Hydric Sulphostannate, Stannic Sulphydrate, or *Sulphostannic Acid,* $H^2Sn^{iv}S^3 = H^2S.SnS^2$, is obtained, by treating the solution of an alkaline sulphostannate with a dilute acid, as a yellow precipitate, which becomes dark-coloured on exposure to the air. (Kühn.)

Sulphostannate of Ammonium is obtained by dissolving stannic sulphide in monosulphide of ammonium, or stannous sulphide, stannous oxide, or stannous hydrate in polysulphide of ammonium.—The *potassium-salt* is obtained in like manner; on mixing its aqueous solution with alcohol, a dark-brown, heavy, oily liquid separates, having nearly the composition $K^2SnS^3.10H^2O$; this compound gives off all its water at 100°.—The *sodium-salt*, $Na^2SnS^3.2H^2O$, forms yellow glassy crystals, whose dominant faces belong to the regular octahedron. A solution of stannous sulphide and sulphur in monosulphide of sodium, deposits colourless monoclinic crystals, resembling gypsum, and containing $Na^2S.Na^2SnS^3.12H^2O$. Höring obtained a similarly crystallised salt containing $Na^2SnS^3.7H^2O$.—The *sulphostannates of barium, calcium,* and *strontium,* obtained by precipitation, are sparingly soluble in water.

TIN, SULPHOCHLORIDE and **SULPHO-IODIDE OF.** (See pp. 809, 814.)

TINCAL. Crude borax, as it is imported from Asia, in yellow greasy crystals. (See BORATES, i. 646.)

TIN-ORE. Native stannic oxide (p. 816).

TINPLATE, or *Tinned Iron-plate.*—An alloy of 2 pts. iron and 1 pt. tin, obtained by heating the two metals together to redness. (See IRON, iii. 370; also *Ure's Dictionary of Arts,* &c. iii. 897.)

TIN-PYRITES. *Stannine. Bell-metal ore. Sulphuret of Tin. Étain sulfuré. Zinnkies.*—A cuproso-ferrous sulphostannate, sometimes also containing zinc, occurring in Cornwall, and at Zinnwald in Bohemia, in cubical forms, but rarely in distinct crystals, mostly massive, and imbedded in crystallo-granular aggregations, with traces of cleavage of the cube and rhombic dodecahedron, and with uneven to small conchoïdal fracture. Hardness = 4·0. Specific gravity = 4·3 to 4·5. It is opaque, with metallic lustre, yellowish-steel-grey colour inclining to brass-yellow, and black streak. Before the blowpipe, on charcoal, it melts to a grey brittle bead, containing copper and iron, and surrounded by a white deposit of stannic oxide. The bead gives, with sodic carbonate and borax, a pale, not perfectly malleable button of copper; when heated in a tube, it gives off sulphurous anhydride, together with a white fume. Nitric acid decomposes it easily, forming a blue solution, with separation of sulphur and stannic oxide.

Analyses:—*a.* From Whealrock, Cornwall (Klaproth, *Beiträge,* v. 298).—*b.* From the same (Kudernatsch, Pogg. Ann. xxxix. 146).—*c.* From St. Michael's Mount, Cornwall (Johnston, Rep. Geol. Cornwall, &c., 1839).—*d.* From the same (Mallet, Sill. Am. J. [2], xvi. 33).—*e.* From Zinnwald (Rammelsberg, Pogg. Ann. lxxxviii. 607):

	a.	*b.*	*c.*	*d.*	*e.*
Sulphur	30·5	29·64	29·93	29·46	29·05
Tin	26·5	25·55	31·62	26·85	25·65
Copper	30·0	29·39	23·55	29·18	29·38
Iron	12·0	12·44	4·79	6·73	6·24
Zinc	. .	1·77	10·11	7·26	9·66
Gangue	. .	1·02	. .	0·16	
	99·0	99·81	100·00	99·64	99·98

These analyses lead to the formula $Cu^2M''Sn^{iv}S^4 = \left.\begin{matrix}Cu^2S\\M''S\end{matrix}\right\}SnS^2$, or $(2Cu^2S.SnS^2).(2M''S.SnS^2)$, where M'' denotes Fe and Zn.

TIN-RADICLES, ORGANIC. The general properties and relations of these bodies have been described in the article ORGANO-METALLIC BODIES (iv. 219, 227). It is there explained that organo-tin compounds may be divided into three groups, analogous in composition to the oxides of tin, and represented by the following formulæ, in which R denotes a monatomic alcohol-radicle:

$$Sn''R^2. \qquad 2Sn'''R^3. \qquad Sn^{iv}R^4.$$

Moreover, one atom of alcohol-radicle in compounds of the second group, and one or two atoms in those of the third group, may be replaced by negative radicles, such as chlorine. Hence arise the following series of organo-tin compounds (R+ denoting an alcohol-radicle, and R− a negative radicle like chlorine):

$$\underset{\text{Stannous compounds.}}{\overset{\text{First Series.}}{Sn''\left\{\begin{matrix}R+\\R+\end{matrix}\right.}} \qquad \underbrace{\overset{\text{Second Series.}}{2Sn'''\left\{\begin{matrix}R+\\R+\\R+\end{matrix}\right.} \qquad \overset{\text{Third Series.}}{2Sn'''\left\{\begin{matrix}R+\\R+\\R-\end{matrix}\right.}}_{\text{Stannoso-stannic compounds.}}$$

$$\underbrace{\overset{\text{Fourth series.}}{\mathrm{Sn^{iv}}\begin{cases}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+\end{cases}}\qquad\qquad \overset{\text{Fifth series.}}{\mathrm{Sn^{iv}}\begin{cases}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}-\end{cases}}\qquad\qquad \overset{\text{Sixth series.}}{\mathrm{Sn^{iv}}\begin{cases}\mathrm{R}+\\ \mathrm{R}+\\ \mathrm{R}-\\ \mathrm{R}-\end{cases}}}_{\text{Stannic compounds.}}$$

In the stannic compounds the atomicity of the tin is fully satisfied: hence these bodies cannot take up any other radicle (such as oxygen, chlorine, &c.) by direct combination, but only by substitution for one or more atoms of alcohol-radicles; in other words, they do not themselves act as radicles. In the stannous compounds, on the contrary, there are two units of atomicity still unsatisfied, and in the stannoso-stannic compounds one such unit: hence these bodies are capable of acting as radicles, taking up chlorine, oxygen, &c. directly, and being thereby converted into stannic compounds. The stannoso-stannic compounds are evidently monatomic; the stannous compounds are always diatomic, uniting with 2 at. chlorine, iodine, &c., or 1 at. oxygen, sulphur, &c., to form stannic compounds; there is no known instance of an organo-stannous compound taking up only 1 at. of a monatomic radicle, to form a stannoso-stannic compound (iv. 227).

Organo-tin compounds have been obtained, containing methyl, ethyl, and amyl. The ethyl-compounds have been most completely studied, and will be most conveniently described first.

a. ETHYL-COMPOUNDS: STANNETHYLS.[*]

Three compounds are known, containing only tin and ethyl, viz.:

Stannous ethide, or Stannodiethyl, $\mathrm{Sn''(C^2H^5)^2}$.

Stannoso-stannic ethide, or Stannotriethyl, $\mathrm{\overset{\prime\prime\prime}{Sn}{}^2(C^2H^5)^6}$.
Stannic ethide, or Stannotetrethyl, $\mathrm{Sn^{iv}(C^2H^5)^4}$.

The first and second of these compounds, as already observed, act as organic radicles, taking up oxygen, chlorine, &c., and forming compounds which may be regarded either as salts of these same radicles, or as stannic compounds containing ethyl and negative radicles:—

$$\mathrm{Sn''(C^2H^5)^2]''.I^2]} \quad = \quad \mathrm{Sn^{iv}}\begin{cases}\mathrm{(C^2H^5)^2}\\ \mathrm{I^2}\end{cases}$$

Stannodiethyl-iodide. Stannic di-iododiethide.

$$\mathrm{[Sn''(C^2H^5)^2]''.O} \quad = \quad \mathrm{Sn^{iv}}\begin{cases}\mathrm{(C^2H^5)^2}\\ \mathrm{O}\end{cases}$$

Stannodiethyl-oxide. Stannic oxydiethide.

$$\mathrm{[Sn''(C^2H^5)^2]''.SO^4} \quad = \quad \mathrm{Sn^{iv}}\begin{cases}\mathrm{(C^2H^5)^2}\\ \mathrm{(SO^4)''}\end{cases}$$

Stannodiethyl-sulphate. Stannic sulphatodiethide.

$$\mathrm{[Sn'''(C^2H^5)^3.I} \quad = \quad \mathrm{Sn^{iv}}\begin{cases}\mathrm{(C^2H^5)^3}\\ \mathrm{I}\end{cases}$$

Stannotriethyl-iodide. Stannic iodotriethide.

$$\mathrm{[\overset{\prime\prime\prime}{Sn}{}^2(C^2H^5)^6]''.S} \quad = \quad \mathrm{\overset{iv}{Sn}{}^2}\begin{cases}\mathrm{(C^2H^5)^6}\\ \mathrm{S''}\end{cases}$$

Stannotriethyl-sulphide. Stannic sulphotriethide.

$$\mathrm{[\overset{\prime\prime\prime}{Sn}{}^2(C^2H^5)^6]''.(CO^3)''} \quad = \quad \mathrm{\overset{iv}{Sn}{}^2}\begin{cases}\mathrm{(C^2H^5)^6}\\ \mathrm{(CO^3)''}\end{cases}$$

Stannodiethyl-carbonate. Stannic carbonatodiethide.

Löwig has also described a number of stannethyls, which cannot be included in either of the preceding groups; they are represented by the following formulæ, using the old atomic weights, $C = 6$, $Sn = 59$:—

Acetostannethyl, $Sn^4(C^4H^3)^3$.
Ethstannethyl, $Sn^4(C^4H^5)^5$.
Radicle not named, $Sn^6(C^4H^5)^4$.
Methylene-stannethyl, $Sn^2(C^4H^5)^2$.
Ethylene-stannethyl, $Sn^4(C^4H^5)^4$.

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[*] Frankland, Phil. Trans. 1852; Ann. Ch. Pharm. lxxxv. 329; cxi. 44; Jahresb. 1852, p. 569 1859, p. 411.—Löwig, Ann. Ch. Pharm. lxxxiv. 308; Jahresb. 1852, p. 577.—Cahours and Riche, Ann. Ch. Pharm. lxxxiv. 333; Jahresb. 1852, p. 576.—Buckton, Ann. Ch. Pharm. cix. 218; cxii. 220; Jahresb. 1858, p. 392; 1859, p. 409.—Cahours, Ann. Ch. Pharm. cxiv. 227, 354; cxxii. 48; Jahresb. 1859, p. 415; 1861, p. 549.—Kulmiz, J. pr. Chem. lxxx. 60; Jahresb. 1860, p. 375.—Strecker, Ann. Ch. Pharm. cv. 306; cxxiii. 365; Jahresb. 1858, p. 387; 1862, p. 398.

The last two are polymeric with stannodiethyl, *$Sn(C^4H^5)$*, according to Löwig. All these radicles are said to unite with 1 at. chlorine, bromine, iodine, &c.

Kekulé (Ann. Ch. Pharm. cxix. 190) supposes these anomalous stannethyl-compounds to be derived from the more simply-constituted radicles above mentioned, by substitution of iodine, chlorine, &c. for ethyl: thus, Löwig's iodide of acetostannethyl, $Sn^2(C^2H^5)^3I$, might be derived, in this manner, from a double molecule of stannodiethyl, $Sn^2(C^2H^5)^4$; and his iodide of ethstannethyl, $Sn^2(C^2H^5)^5I$, in like manner, from a double molecule of stannotriethyl, $Sn^2(C^2H^5)^6$.

Strecker has pointed out that Löwig's methylene- and ethylene-stannethyl are most probably identical with stannethyl, and that the compounds described by Löwig as iodide of methylene- and ethylene-stannethyl are oxyiodides of stannethyl, containing $Sn^2(C^2H^5)^4I^2O$ and $Sn^2(C^2H^5)^4I^2O^3$—compounds which Strecker has actually obtained by other processes (p. 827). In bodies whose molecular weights are as high as those of the stannethyl-compounds, the quantities of oxygen indicated by these formulæ would make but little difference in the percentage of the other elements.

It must further be observed, that the existence of these anomalous stannethyls is by no means well established. Löwig never succeeded in isolating them completely, or in preparing their compounds in a pure state; and Cahours was never able to obtain them at all, however much he might vary the proportions of the materials.

Preparation of Stannethyls.—1. Finely-divided tinfoil is introduced, together with three times its weight of ethylic iodide, into a strong glass tube, which is sealed and exposed to sunshine. A slow reaction then takes place, requiring several weeks' exposure to the summer sun for its completion; it may, however, be greatly accelerated by concentrating the rays with a parabolic reflector, and at the same time keeping the tube cool by immersion in water, or in solution of cupric sulphate; the reaction is then completed in a few days. The product solidifies to a crystalline mass, consisting mainly of stannic di-iododiethide, $Sn^{iv}(C^2H^5)^2I^2$, with small quantities of stannous iodide and stannic iodotriethide, $Sn^{iv}(C^2H^5)^3I$ (Frankland):

$$2C^2H^5I + Sn = Sn(C^2H^5)^2I^2.$$
$$3C^2H^5I + Sn^2 = Sn(C^2H^5)^3I + SnI^2.$$

2. A mixture of 1 pt. finely-cut tinfoil and 2½ to 3 pts. ethylic iodide, is enclosed in a sealed tube, and heated to 150° in an oil-bath for 20 or 30 hours. After *cooling*, the contents of the tube are found to consist partly of colourless crystals of stannic di-iododiethide (iodide of stannodiethyl), partly of yellowish crystals of stannic iodotriethide (iodide of stannotriethyl). On decanting the liquid from the crystals, and distilling, a small quantity of ethylic iodide passes over first; then, at 230°, the stannic iodotriethide; and at 245° the stannic di-iododiethide, the residue consisting of stannous iodide. (Cahours; Riche.)

3. Stannide of sodium, prepared by fusing 6 pts. of tin with 1 pt. of sodium, is finely pulverised, and mixed with quartz-sand in the proportion of 1 pt. of the alloy to 1—1½ pts. of sand; the mixture quickly introduced into a number of glass flasks of 3 or 4 ounces' capacity; and a quantity of ethylic iodide added, sufficient to form a thick paste: the flask is then briskly shaken, and a distillation-tube adapted to it. The action commences in a few minutes, and is completed the more quickly in proportion as the alloy is richer in sodium. The heat which it developes is sufficient to cause the excess of ethylic iodide to distil over, after which the flask, while yet warm, is closed airtight; after the mixture has cooled, the treatment with iodide of ethyl is renewed, and the same operation repeated till a sample of the contents of the flask no longer gives off hydrogen when thrown into water. The dry, dusty, yellowish, stinking mass, obtained in this manner from several flasks, is then transferred to a bottle filled with ether (from 4½ to 5 pounds to the contents of 16 flasks), left to stand for an hour or two, and frequently shaken; after which the dark-brown ethereal solution is poured into a bottle filled with carbonic anhydride, and left to stand for half an hour or an hour, whereupon, especially if there were any air in the bottle, a brown substance, which dries up in the air to a white inodorous mass, separates out. The ethereal solution is then transferred to a retort, mixed with about $\frac{1}{10}$ of its bulk of alcohol, and the ether is completely distilled off. There then remains a dark turpentine-like mass [consisting, according to Löwig, of the radicle $Sn^3(C^2H^5)^4$], and an alcoholic solution, which, when decanted and left at rest, deposits a large quantity of yellow oil, frequently separating, after some time, into two layers, the lower of which consists mainly of stannous ethide, $Sn''(C^2H^5)^2$, or stannodiethyl. The alcoholic liquid decanted from the yellow oil deposits, on addition of water, a nearly colourless oil, the first precipitated portion of which consists mainly of stannous

ethide, and the last of stannosostannic ethide or stannotriethyl; while the intermediate portions contain other radicles (p. 825), which, after conversion into iodides, may be separated by fractional crystallisation (Löwig). For Löwig's method of separating these supposed radicles, see *Gmelin's Handbook*, ix. 93.

Stannous Ethide, or **Stannodiethyl,** $Sn''(C^2H^5)^2$.—The method last described yields this radicle comparatively pure. The best method of obtaining it however is to immerse a strip of zinc-plate in a warm solution of stannodiethyl-chloride; it then collects at the bottom of the vessel, as a thick yellowish oil. (Frankland.)

Stannous ethide would probably be colourless when quite pure. It has a specific gravity of 1·558 at 15°, does not solidify at $-12°$, and cannot be distilled without decomposition. It has an extremely pungent odour, stronger than that of any of its compounds. It is insoluble in water, but soluble in *alcohol*, and still more soluble in *ether*.—It absorbs *oxygen* from the air, but does not fume or take fire; it reduces *nitrate of silver* immediately, with separation of black metallic silver; and unites directly with *chlorine*, *bromine*, and *iodine*.—With *hydrochloric*, *hydriodic*, *hydrobromic*, and *hydrofluoric acids*, it forms haloïd salts, with evolution of hydrogen. When heated to 150°, it boils, and is resolved into stannic ethide, $Sn(C^2H^5)^4$, which distils over, and metallic tin.

Compounds of Stannethyl.—These compounds, which, as already observed, may be regarded as belonging to the stannic type, are produced either by direct combination, or by double decomposition from the iodide.

BROMIDE, $Sn(C^2H^5)^2Br^2$.—Produced by treating an alcoholic solution of stannodiethyl with bromine, or by dissolving the oxide in hydrobromic acid; also, together with other compounds, by heating ethylic bromide with tin to 150°. It forms long white needles, having a faint camphorous odour, melts when gently heated, and distils without decomposition at 232°. Its vapour-density (taken at 295°) is 11·64; by calculation (2 vols.) = 11·74. It is soluble in water and alcohol, and especially in ether. (Löwig; Cahours.)

CHLORIDE, $Sn(C^2H^5)^2Cl^2$.—Obtained, in long colourless needles, by dissolving the oxide in dilute hydrochloric acid, and evaporating at a gentle heat. It melts at 60°, sublimes when slightly warmed, and boils without decomposition at 220°. Vapour-density = 8·71 and 8·62 at 268°—282° (Cahours); calc. = 8·62. It has a stronger odour than the bromide, is moderately soluble in boiling water, more easily in alcohol and in ether. (Löwig; Frankland; Cahours.)

When ammonia is added by drops to a boiling alcoholic solution of the chloride, till a permanent precipitate begins to form, this precipitate redissolved by addition of a little more of the stannodiethyl-chloride, and the liquid left to cool, white shining laminæ are deposited, consisting of stannodiethyl-oxychloride, $Sn^2(C^2H^5)^4OCl^2$. (Strecker.)

FLUORIDE, $Sn(C^2H^5)^2F^2$.—Obtained, in fine crystals, by evaporating the solution of stannethyl-oxide in hydrofluoric acid.

IODIDE, $Sn(C^2H^5)^2I^2$.—This compound is the direct product of the action of ethylic iodide upon tin, or upon sodium-stannide containing a small proportion of sodium, and is likewise easily produced by the action of iodine on stannodiethyl in ethereal solution. It forms colourless, inodorous, needle-shaped crystals, often several inches long, melts at 42°, sublimes at 160° in shining needles or laminæ, and boils, without decomposition, at 245°. It dissolves sparingly in cold, more easily in warm water, also in cold alcohol and ether. (Löwig; Frankland; Cahours.)

The warm aqueous solution of the iodide, mixed with a small quantity of ammonia, yields, on cooling, an oxyiodide, $Sn^4(C^2H^5)^8I^2O^3$, in hard prismatic crystals, slightly soluble in water, more soluble in alcohol or ether. The same crystals are obtained by boiling oxide of stannethyl with an alcoholic solution of the iodide. (Strecker.)

Iodocyanide, $Sn(C^2H^5)^2CyI$.—Produced by heating equivalent quantities of stannethyl-iodide and silver-cyanide with a small quantity of anhydrous alcohol, in sealed tubes immersed in a salt-bath. By evaporating the filtered solution, it is obtained as a crystalline powder.

OXIDE, $Sn(C^2H^5)^2O$.—Obtained, as a white powder, by evaporating an ethereal solution of stannodiethyl in contact with the air, or by precipitating a solution of a stannethyl-salt with ammonia. It is tasteless, inodorous, not volatile, takes fire when heated in contact with the air, burning with a bright flame, and giving off fumes of stannic oxide. It is insoluble in water and in ammonia, nearly insoluble in alcohol and ether, but dissolves easily in dilute acids and in the fixed alkalis. On distilling it with excess of aqueous potash, stannotriethylic hydrate passes over with the aqueous vapour, and stannate of potassium remains behind:

$$3Sn(C^2H^5)^2O + 2KHO = K^2SnO^3 + 2Sn(C^2H^5)^3(HO).$$

[illegible] stannethyl-oxide at a gentle heat, [illegible] oxychloride, which may be [illegible]

[illegible] $C^2H^5Cl^2$

[illegible] are formed by the [illegible] with silver [illegible] in water, less so in [illegible] like that of mustard [illegible] gradually adding stann[illegible] solidifies to a crys[illegible] evaporation, it is obtained [illegible] partly decomposes, partly [illegible] in alcohol or ether.

[illegible] of silver-cyanate on an [illegible] crystallises on evaporating the solution.

[illegible] is gradually added to dilute form[illegible] formate separates as a thick [illegible] boiling, and when recrystal[illegible]

[illegible] by decomposing the [illegible] dilute nitric acid, and is [illegible] When heated, it melts, decom[illegible] in water and in alcohol

[illegible] is obtained [illegible] nitrate of silver: the solu[illegible] Strecker.)

[illegible] of ammonium[illegible] amorphous powder, insoluble in [illegible]

[illegible] salts. Beautiful crys[illegible] Löwig.)

[illegible] oxide like acetic acid; a [illegible] in hard prisms on cooling.

[illegible] powder on passing sulphydric [illegible] has a pungent nauseating [illegible] in dilute acids and in [illegible] and sulphide of potassium; [illegible] on addition of acids. [illegible]

SULPHO[illegible]ANATE. [illegible]—[illegible] prolonged digestion of stann[illegible] of silver. The solution, con[illegible] have an alliaceous odour, [illegible] products.

Stannosostannic Ethide, or **Stannotriethyl,** [illegible] $(C^2H^5)^3$]. *Sesquistan-nethyl.* [illegible]—The preparation [illegible] by Löwig's method has been already described (p. 826). [illegible] in excess to an alloy of 80 pts. [illegible] 20 pts. sodium in a retort, and after the spontaneous reaction is over, heats [illegible] with a small quantity of [illegible] in strong glass tubes for twenty hours to 120°. The contents of the tubes, when cold, are added to pure ether, and after twenty-four hours' digestion, the solution is filtered into vessels filled with carbonic anhydride, whereupon it deposits a white flocculent mass. The solution filtered therefrom is distilled to one-eighth of its original volume; and the residue is mixed with half its volume of ordinary alcohol, and further evaporated, till a clear yellowish oil settles down to the bottom of a viscid colourless liquid. This yellow oil, after washing with alcohol and heating to 170°–180°, constitutes pure stannotriethyl. This compound, according to Kulmiz, is a nearly colourless, heavy, slightly refractive oil, having a peculiar odour like that of rotten fruits. It unites directly with oxygen, chlorine, bromine, and iodine.

Compounds of Stannotriethyl.

These compounds may be regarded as formed by the union of 1 at. iodine, chlorine, &c. with 1 at. of the monatomic radicle $Sn'''(C^2H^5)^3$, or as stannic molecules, in which three of the four units of atomicity of the tin are neutralised by ethyl, and the fourth by a negative radicle (p. 825), the molecule being doubled for compounds containing diatomic negative radicles, such as S, O, SO^4, &c.; *e.g.*:

$$Sn'''(C^2H^5)^3.Cl \quad = \quad Sn^{iv}\left\{\begin{matrix}(C^2H^5)^3\\Cl\end{matrix}\right.$$

Stannotriethyl-chloride. **Stannic chloro-triethide.**

$$[Sn'''(C^2H^5)^3]^2.SO^4 \quad = \quad \overset{''''}{Sn}{}^2\left\{\begin{matrix}(C^2H^5)^6\\(SO^4)''\end{matrix}\right.$$

Stannotriethyl-sulphate. **Stannic sulphato-triethide.**

Their modes of formation are analogous to those of the stannethyl-compounds.

Bromide, $Sn(C^2H^5)^3Br$.—This salt is most easily obtained by treating the oxide with hydrobromic acid. It is a colourless, mobile, strongly refracting liquid, of specific gravity 1·630, and boiling at 223°. It has a very pungent odour, like that of mustard-oil, dissolves readily in ether and in alcohol, even when dilute, but very sparingly in water (Löwig; Cahours; Kulmiz). Vapour-density = 9·924 (Cahours); calc. = 9·60.

Chloride, $Sn(C^2H^5)^3Cl$.—Obtained by dissolving the oxide in hydrochloric acid, or (more readily) by adding that acid to an aqueous solution of the sulphite. It is a transparent, colourless, strongly refracting liquid, having a very powerful and suffocating odour. Specific gravity = 1·428 at 8° (Cahours), 1·320 (Kulmiz). Boils at 209°. Vapour-density (obs.) = 8·430 at 285°; calc. = 8·33. At 0° it solidifies in colourless prisms. According to Kulmiz, it forms, with *platinic chloride*, two crystalline compounds, containing $Sn^2(C^2H^5)^6Cl^2.PtCl^4$ and $Sn(C^2H^5)^3Cl.PtCl^4$, respectively. It also forms crystalline compounds with *auric* and *mercuric chloride*.

Cyanide, $Sn(C^2H^5)^3Cy$.—When stannotriethyl-iodide and silver-cyanide are gently heated together in a retort, this compound sublimes in snow-white crystals, which may be freed from a grey substance, often adhering to them, by solution in alcohol and spontaneous evaporation. It forms silky flexible prisms, which melt when gently heated, and sublime without decomposition. When quickly heated it suffers partial decomposition. It is nearly inodorous in the cold, but when heated, it emits an odour like that of prussic acid and the stannotriethyl-compounds together.

Hydrate, $\left.\begin{matrix}Sn'''(C^2H^5)^3\\H\end{matrix}\right\}O = Sn^{iv}(C^2H^5)^3(HO)$.—This compound is separated from solutions of stannotriethyl-salts by caustic potash, but generally remains dissolved. It may, however, be withdrawn from the solution by agitation with ether, and obtained in the crystalline form by leaving the ether to evaporate. When a solution of stannotriethyl-iodide is distilled with excess of potash, the hydrate passes over with the aqueous vapour, and solidifies in the crystalline form on cooling; and even when the alkaline solution is gently heated in a beaker-glass, the hydrate gradually sublimes, filling the entire space with slender crystals, which form a mass like cotton-wool. To obtain the hydrate from a mixture of the iodides of stannethyl and stannotriethyl—such as is ordinarily produced by the action of tin on ethylic iodide—the mixture is dissolved in alcohol; silver-oxide is added as long as silver-iodide is thereby produced; the solution containing the hydrate of stannotriethyl is filtered from the precipitate consisting of a mixture of stannethyl-oxide and silver-iodide; and the filtrate evaporated over oil of vitriol.

Stannotriethyl-hydrate forms colourless prismatic crystals, moderately soluble in alcohol, either anhydrous or hydrated, easily in ether. The solutions have a strongly alkaline reaction and caustic taste, precipitate most of the heavy metals from their solutions as oxides or hydrates, and absorb carbonic acid from the air. The hydrate neutralises acids completely, forming with most of them crystalline salts.

Iodide, $Sn(C^2H^5)^3I$.—This compound is produced in small quantity when tin is heated to 150° with ethylic iodide, more abundantly when an alloy of tin and sodium is used; also, together with ethylic iodide, by the action of iodine on stannic ethide:

$$Sn(C^2H^5)^4 + I^2 = C^2H^5I + Sn(C^2H^5)^3I.$$

The best mode of preparing it is to treat an alloy of 7 pts. tin and 1 pt. sodium with ethylic iodide, whereupon a brisk action takes place, accompanied by great rise of temperature. As soon as this action is over, the residue, mixed with ethylic iodide to a thin paste, is enclosed in sealed tubes, and heated, for eighteen or twenty hours, to 125°, or at most 130°. The tubes, when cold, are opened, the contents treated with ether, and the filtered solution evaporated, after addition of a little alcohol. On leaving the ether to evaporate, a yellowish oil separates, the quantity of which increases on addition of water; and on distilling this oil by itself, pure stannotriethyl-iodide passes over, between 230° and 235°. (Cahours.)

Stannotriethyl-iodide is a colourless, heavy, strongly refracting liquid, of specific gravity 1·833 at 22°, and boiling without decomposition between 235° and 238° (Cahours). It solidifies in a mixture of carbonic anhydride and ether. It has a pungent odour, attacking the nose and eyes like oil of mustard. It mixes in all proportions with absolute alcohol and with ether, dissolves sparingly in water, easily in hydrated alcohol. It dissolves iodine, with brown colour in the cold; but on heating the solution the free iodine disappears, and iodide of stannethyl is formed, together with iodide of ethyl.

Stannotriethyl-iodide absorbs *ammonia-gas*, forming the compound $Sn(C^2H^5)^3I.2NH^3$, which may be obtained in thin prisms, by adding a solution of the iodide to anhydrous alcohol saturated with ammonia-gas, warming the liquid for a few hours in the water-bath, and then leaving it to cool. It likewise forms crystalline compounds, of analogous composition, with *ethylamine*, *amylamine*, and *aniline*.

OXIDE, $Sn^2(C^2H^5)^6O$.—Obtained, by prolonged heating of the hydrate to a temperature near its boiling-point, as a transparent oil, which, when mixed with a small quantity of water, is reconverted into the crystalline hydrate. (Cahours.)

OXYGEN-SALTS.—These salts are obtained by dissolving the hydrate, oxide, or carbonate of stannotriethyl in the aqueous acids, or by decomposing the iodide with silver-salts. They are mostly crystalline, and dissolve readily in water, alcohol, and ether.

Acetate, $Sn(C^2H^5)^3(C^2H^3O^2)$.—Prepared by dissolving the oxide in acetic acid. Slightly soluble in water, easily in alcohol, whence it separates, by spontaneous evaporation, in tufts of white silky needles. It melts at a gentle heat, sublimes at a somewhat higher temperature in snowy flocks, and boils without decomposition at 230°. (Kulmiz; Cahours.)

Arsenate, $Sn(C^2H^5)^3(AsO^4)$.—White crystalline mass, soluble in alcohol, and crystallising therefrom in tufts of shining needles. (Kulmiz.)

Benzoate, $Sn(C^2H^5)^3(C^7H^5O^2)$.—Obtained by double decomposition from the iodide. Long, transparent, highly lustrous prisms, which melt at 80°, and sublime without decomposition at a higher temperature. Sparingly soluble in water, easily in alcohol, even when dilute. (Kulmiz.)

Butyrate, $Sn(C^2H^5)^3(C^4H^7O^2)$.—Thin shining needles, sublimable without decomposition, slightly soluble in cold water, moderately soluble in alcohol, especially when warm.

Carbonate, $Sn^2(C^2H^5)^6(CO^3)$.—The hydrate absorbs carbonic acid from the air during the evaporation of its alcoholic solution. The alcoholic solution of the sulphate, mixed with carbonate of ammonium or carbonate of sodium, deposits stannotriethyl-carbonate as a dazzling-white crystalline powder. (Kulmiz.)

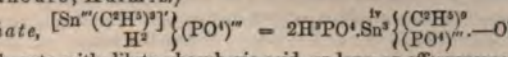
Cyanate, $Sn(C^2H^5)^3(CNO)$.—Prepared by gradually adding dry cyanate of silver to an alcoholic solution of stannotriethyl-chloride, as long as the liquid is thereby coloured yellow. The filtrate left to evaporate yields the salt in tufts of thin prisms, having a silky lustre. It is moderately soluble in alcohol and in ether, is converted into carbonate by exposure to moist air, gives off carbonic anhydride when treated with strong acids, and ammonia when boiled with potash.

When ammonia-gas is passed into the alcoholic solution of this salt, and the liquid left to evaporate, there remains a substance which dissolves partially in alcohol; and this solution yields, by evaporation, long colourless prisms, regarded by Kulmiz and Cahours as stannotriethyl-carbamide, $\left.\begin{matrix}(CO)''\\H^3\\Sn(C^2H^5)^3\end{matrix}\right\}N^2$; but they are, perhaps, only a mixture of carbamide (urea) with a salt of stannotriethyl. They have not been analysed.

Formate, $Sn(C^2H^5)^3(CHO^2)$.—Thin prisms, having a silky lustre when dry, melting between 50° and 60°, and then subliming completely; very soluble in strong alcohol. (Cahours; Kulmiz.)

Nitrate, $Sn(C^2H^5)^3(NO^3)$.—Prepared by mixing an alcoholic solution of the hydrate with nitric acid, then adding ether and enough water to cause the liquid to separate into two layers, the upper of which contains the nitrate, and leaves it as a syrupy mass when evaporated. When cold it forms a transparent varnish, which dissolves easily in alcohol and ether, and burns away, when heated, with a faint light, but without detonation. (Löwig.)

Oxalate, $Sn^2(C^2H^5)^6(C^2O^4)''$.—A solution of oxalic acid in dilute alcohol takes up a large quantity of stannotriethyl-hydrate, and deposits the oxalate, on evaporation, in shining colourless prisms, sparingly soluble in cold, easily in warm water, alcohol, or ether. It is inodorous at ordinary temperatures, but decomposes when heated above 100°. (Cahours; Kulmiz.)



Phosphate, $\left.\begin{matrix}[Sn'''(C^2H^5)^3]' \\ H^2\end{matrix}\right\}(PO^4)''' = 2H^3PO^4.\overset{iv}{Sn^3}\left\{\begin{matrix}(C^2H^5)^9 \\ (PO^4)'''\end{matrix}\right.$.—Obtained by treating the carbonate with dilute phosphoric acid as long as effervescence is produced, as a white powder, which dissolves in very dilute alcohol, and separates, on evaporation, in tufts of transparent shining needles. It is moderately soluble in warm water, very soluble in dilute alcohol, slightly in ether. The solutions have an acid reaction. (Kulmiz.)

Sulphate, $Sn^2(C^2H^5)^6(SO^4)''$.—Separates from alcoholic solution in nearly transparent six-sided prisms with six-sided pyramidal summits (Kulmiz). It is more soluble in cold than in warm water, so that a solution saturated in the cold solidifies almost completely when heated (Buckton). It is easily soluble in alcohol. (Cahours.)

Tartrates.—The *neutral salt*, $Sn^2(C^2H^5)^6(C^4H^4O^6)''$, is obtained by treating the carbonate with excess of tartaric acid, dissolving the crystalline deposit in dilute alcohol, and leaving the solution to evaporate. It forms cubic crystals, which melt and decompose at a rather high temperature.—An *acid salt*, $Sn^2(C^2H^5)^6(C^4H^4O^6)''.C^4H^6O^6 + 2aq.$, is contained in the mother-liquor of the neutral salt; and on leaving this liquid to evaporate completely, washing the crystalline residue with a little water to remove excess of tartaric acid, then dissolving it in aqueous alcohol, and leaving the solution to evaporate, the acid tartrate separates in well-defined, shining, rhombic crystals, moderately soluble in water, easily in dilute alcohol. (Kulmiz.)

A few other oxysalts of stannotriethyl have been prepared, but not accurately investigated.—The *bromate* and *iodate*, formed by the action of bromine or iodine on an alcoholic solution of stannotriethyl-hydrate, separate in small shining crystals, which detonate slightly when heated (Löwig).—The *caproate*, *caprylate*, and *valerate* resemble the acetate and butyrate. (Cahours).

SULPHIDE, $Sn^2(C^2H^5)^6S$.—When an alcoholic solution of the hydrate is divided into two equal parts, one portion saturated with sulphydric acid, and the second portion added after the excess of sulphydric acid has been expelled by evaporation, the sulphide separates as a heavy oil, which may be dried over sulphuric acid. It is transparent, has an amber-yellow colour, strong refracting power, and a fetid odour. (Cahours; Kulmiz.)

SULPHYDRATE, $Sn(C^2H^5)^3(HS)$.—Obtained by saturating a solution of the hydrate in absolute alcohol with sulphydric acid gas, and evaporating, in colourless needle-shaped crystals having an odour of mercaptan. (Cahours.)

SULPHOCYANATE, $Sn(C^2H^5)^3(CNS)$.—Obtained by heating an alcoholic solution of the iodide with excess of silver-sulphocyanate in the water-bath, and evaporating, as a viscid, slightly amber-yellow mass, which gradually becomes crystalline. It melts when heated, and solidifies again in the crystalline state on cooling. It dissolves in alcohol and ether, and exhibits the general reactions of the two sulphocyanates. (Cahours.)

Stannic Ethide, or **Stannotetrethyl,** $Sn^{iv}(C^2H^5)^4$.—This compound is produced by the action of zinc-ethyl on iodide of stannodiethyl or iodide of stannotriethyl, the iodine being replaced by ethyl:

$$Sn(C^2H^5)^2I^2 + Zn''(C^2H^5)^2 = ZnI^2 + Sn(C^2H^5)^4.$$
$$2Sn(C^2H^5)^3I + Zn(C^2H^5)^2 = ZnI^2 + 2Sn(C^2H^5)^4.$$

It is also formed by the action of zinc-ethyl on stannic chloride (Buckton), and lastly in the distillation of stannous ethide, metallic tin being separated at the same time.

To prepare it, crystallised stannodiethyl-iodide (stannic di-iododiethide) is gradually added to an ethereal solution of zinc-ethyl, the crystals then dissolving with moderate rise of temperature, and a syrupy liquid being ultimately obtained. If this liquid —which should contain an excess of zinc-ethyl—be then distilled, the boiling-point quickly rises from 70° to 180°, and the greater part of the product passes over between 180° and 200°, while zinc-iodide and a small quantity of zinc-ethyl remain in the retort. The distillate contains a little zinc-ethyl, which must be decomposed by water, with addition of acetic acid, and the heavy oil which then settles down is separated from the supernatant watery liquid, dried over chloride of calcium, and rectified. (Frankland.)

Stannic ethide is a transparent colourless liquid, of specific gravity 1·87 at 23°. It remains liquid at −13°, and boils at 181°. Vapour-density, obs. = 8·021 (Frankland); calc. = 8·108. It has a faint ethereal odour, and a somewhat metallic but not unpleasant taste. It is inflammable, and burns with a dark-blue-edged flame, emitting white fumes of stannic oxide. In oxygen-gas it burns with a dazzling light.

Stannic ethide dissolves *iodine* with brown colour, which gradually disappears. If the addition of iodine be continued as long as the brown colour disappears without aid of heat, and the liquid be then distilled, ethylic iodide and afterwards stannotriethyl-iodide pass over (Buckton; Frankland). When the action of the iodine is assisted by a gentle heat, the decomposition goes further in the same direction, and a mixture of the iodides of ethyl and stannodiethyl is obtained (Cahours). Lastly, when stannic ethide is somewhat strongly heated with excess of iodine in a sealed tube, iodide of ethyl is produced, together with red iodide of tin. (Cahours.)

Stannic ethide reacts in a similar manner with *bromine*.

Stannic ethide is not decomposed by *water*, neither is it acted on by strong *hydrochloric acid* in the cold; but on heating the mixture over mercury to 80° or 90°, bubbles of hydric ethide are very slowly evolved, and stannotriethyl-chloride is produced (Frankland):

$$Sn(C^2H^5)^4 + HCl = C^2H^5.H + Sn(C^2H^5)^3Cl.$$

According to Cahours, the reaction takes place more quickly at 100°; and if it be longer continued, with a larger excess of hydrochloric acid, crystallised stannethyl-chloride is produced.

Stannic ethide mixes with *stannic chloride*, producing considerable rise of temperature, and forming chloride of stannotriethyl:

$$3Sn(C^2H^5)^4 + SnCl^4 = 4Sn(C^2H^5)^3Cl.$$

It also mixes with *chloride of stannethyl*, but without acting chemically upon it, at least at moderate temperatures. (Buckton.)

β. Methyl-compounds: Stannmethyls.[*]

These compounds are analogous in constitution to the stannethyls, which they also resemble, generally, in their properties and modes of formation. Their names and formulæ are as follows:

Stannous methide, or Stannodimethyl, $Sn''(CH^3)^2$.
Stannoso-stannous methide, or Stannotrimethyl, $2[(Sn''(CH^3)^3]$.
Stannic methide, or Stannotetramethyl, $Sn^{iv}(CH^3)^4$.

The first is a diatomic, the second a monatomic radicle; the third, in which the atomicity of the tin is fully satisfied, does not act as a radicle.

There are also tin-compounds of analogous constitution, containing both ethyl and methyl.

Stannous Methide, or **Stannodimethyl,** $Sn''(CH^3)^2$.—This compound is formed by heating methylic iodide with an alloy of 1 pt. sodium and 5 pts. tin, in sealed tubes to 130°. By exhausting the contents of the tubes with ether, and evaporating the solution in an atmosphere of carbonic anhydride, it is obtained, not quite pure, as a heavy oily liquid having a mouldy smell. It is insoluble in water, easily soluble in alcohol and ether, and is resolved by heat into stannic methide and metallic tin. The alcoholic solution forms, with nitrate of silver, a black precipitate of metallic silver.

The compounds of stannodimethyl may be regarded (like those of stannodiethyl) as stannic compounds, in which two out of the four units of atomicity of the tin are satisfied by methyl, and the other two by a negative radicle. They are formed either by direct combination, or from the iodide by double decomposition.

Bromide, $Sn(CH^3)^2Br^2$.—Obtained by treating the oxide with excess of hydrobromic acid, and separates from the concentrated liquid in crystals, which may be purified by recrystallisation from alcohol. They are colourless prisms, isomorphous with the corresponding chloride. The salt boils without decomposition at 208°—210°. It is moderately soluble in water, more easily in alcohol. (Cahours.)

Chloride, $Sn(CH^3)^2Cl^2$.—Separates, on evaporating a solution of the oxide in excess of hydrochloric acid, in fine prisms. It melts at 90°, and boils at 188°—190°. Vapour-density, obs. (at 265) = 7·731; calc. = 7·63. It dissolves in water, more easily in alcohol and in ether. (Cahours)

Iodide, $Sn(CH^3)^2I^2$.—Produced, like the corresponding ethyl-compound, by the action of tin on methylic iodide in sunshine (Frankland), or with aid of heat (Cahours and Riche). To prepare it, 2½ to 3 pts. methylic iodide are heated with 1 pt. of tinfoil to 150°—160°, in sealed tubes, for twelve to fifteen hours. The tubes, after cooling, contain a mixture of a brown liquid and sulphur-yellow crystals, and on subjecting this mixture to fractional distillation, methylic iodide passes over first after which the boiling-point gradually rises to 230°, and at last nothing but red iodide of tin is left. The distillate, on cooling, deposits yellow crystals of stannic di-iododimethide, and the mother-liquor decanted therefrom consists chiefly of stannic iodotrimethide; but if it be again rectified, the portion which last goes over will yield an additional quantity of stannic di-iododimethide. The crystals are pressed between paper, then dissolved in a mixture of alcohol and ether; and by leaving this solution to evaporate in a shallow vessel over oil of vitriol, in a dark place, crystals of considerable size may be obtained.

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[*] Frankland, Ann. Ch. Pharm, lxxxv. 346; Jahresb. 1852, p. 572.—Cahours and Riche, Ann. Ch. Pharm. lxxxviii. 316; Jahresb. 1852, p. 577.—Cahours, Ann. Ch. Pharm. cxiv. 367; Jahresb. 1859, p. 426.

Stannic di-iododimethide, or iodide of stannodimethyl, forms oblique rhombic crystals, which become somewhat opalescent on exposure to the air. It melts at about 30° to a liquid resembling melted sulphur; and by piercing the crust which forms on cooling, and pouring out the still remaining liquid, it may be obtained in well-defined rhombic prisms. Specific gravity = 2·872 (at 22°). It boils regularly at 228°. It dissolves in water, especially when warm, and very easily in alcohol, wood-spirit, acetone, or ether. Ammonia separates white stannethyl-oxide, insoluble in excess of ammonia. (Cahours.)

Oxide, $Sn(CH^3)^2O$.—The precipitate, obtained in the manner just mentioned, forms, when washed with dilute alcohol and dried, a white, amorphous, tasteless powder, insoluble in water, alcohol, ether, and aqueous alkalis. When heated, it decomposes, giving off the odour of stannotrimethyl-oxide. When stannodimethyl-oxide is heated with excess of potash, stannotrimethyl-oxide volatilises with the aqueous vapour, and stannate of potassium remains behind:

$$3Sn(CH^3)^2O + 2KHO = K^2SnO^3 + Sn^2(CH^3)^6O + H^2O.$$

Oxygen-salts.—Most acids dissolve the oxide of stannodimethyl, forming crystallisable salts.—The *formate*, $Sn(CH^3)^2(CHO^2)^2$, crystallises in fine prisms, which, when heated, partly decompose, partly sublime unaltered.—The *butyrate* and *acetate* closely resemble the formate.—The *caprylate* and *valerate* crystallise easily, and are soluble in alcohol.—The *sulphate*, $Sn(CH^3)^2SO^4$, obtained by decomposing the iodide with silver-sulphate, or by dissolving the oxide in a slight excess of dilute sulphuric acid, and evaporating over oil of vitriol, crystallises in colourless prisms, often of considerable size. It is soluble in water, especially when warm, nearly insoluble in alcohol even at the boiling heat. It decomposes completely when heated, emitting a pungent odour. (Cahours.)

Stannosostannic Methide, or **Stannotrimethyl,** $Sn'''(CH^3)^3$.—This radicle is not known in the free state. Its compounds, which may be regarded as stannic molecules containing 3 at. methyl and 1 at. of a negative radicle, are produced by several reactions:—

1. The iodide is formed, together with stannodimethyl-iodide (p. 832) and stannic iodide, by the action of tin on methylic iodide at 130°—160°:

$$6(CH^3)I + Sn^3 = SnI^4 + 2Sn(CH^3)^3I.$$

2. The iodide is formed, together with methylic iodide, by the action of iodine on stannic methide at ordinary temperatures:

$$Sn(CH^3)^4 + I^2 = CH^3I + Sn(CH^3)^3I.$$

3. The oxide is formed, together with stannic oxide, by boiling stannic di-iododimethide with excess of potash:

$$3Sn(CH^3)^2I^2 + 3K^2O = Sn^2(CH^3)^6O + SnO^2 + 6KI.$$

The *iodide*, $Sn(CH^3)^3I$, is best prepared by heating tin with methylic iodide to 150°—160° in sealed tubes, and separating the stannodimethyl-iodide formed at the same time, by repeated rectification. The portion which passes over between 180° and 200°, if rectified till it no longer becomes turbid on cooling, and no longer deposits crystals of stannic iodide, yields pure stannotrimethylic iodide. (Cahours.)

This iodide is a thin colourless liquid, of specific gravity 2·153 at 18°, and boiling at 188°—190°. Vapour-density (at 260°) = 10·325; calc. = 10·049. It has a pungent odour like that of mustard-oil, but not so strong as that of the corresponding ethyl-compound. It remains liquid at the temperature of a mixture of ice and salt, but solidifies immediately at that of a mixture of ether and solid carbonic anhydride. (Cahours.)

Oxide and *Hydrate.*—When the iodide is mixed with excess of potash ley, the hydrate remains dissolved, but passes over on distilling the liquid, and collects in the receiver, together with water, as an oil which solidifies to a crystalline mass; and by pressing this mass between paper, and again rectifying, it may be obtained in colourless transparent prisms. It volatilises without decomposition, but, when heated for some time to a temperature near its boiling-point, it is resolved into water and anhydrous stannotrimethyl-oxide. It is sparingly soluble in water, more soluble in alcohol; the solutions are alkaline, and neutralise the strongest acids.

Oxygen-salts.—These salts are nearly all soluble, crystallise easily, are isomorphous with the corresponding stannotriethyl-salts, and volatilise without decomposition, emitting a pungent odour.

Formate, $Sn(CH^3)^3(CHO^2)$.—Somewhat concentrated formic acid, added to a saturated solution of the oxide, produces a precipitate which redissolves on heating the liquid, more easily on addition of alcohol. The solution, if left to evaporate, yields fine prismatic crystals, which melt at a gentle heat, and sublime without decomposition at a higher temperature. They dissolve easily in alcohol and ether.—The *acetate*, $Sn(CH^3)^3(C^2H^3O^2)$, is prepared like the formate, which it resembles in external characters. It volatilises without decomposition, dissolves easily in alcohol, less easily in water.—The *sulphate*, $\overset{iv}{Sn}{}^2(CH^3)^6(SO^4)''$, crystallises in small, colourless, shining prisms, easily soluble in water and in alcohol. (Cahours.)

Stannic Methide, or Stannotetramethyl, $Sn(CH^3)^4$. *Stannodimethyl. Stannobimethyl.*—This compound is produced by the action of zinc-methyl on stannic di-iododimethide, or stannic iodotrimethide, thus:

$$Sn(CH^3)^2I^2 + Zn(CH^3)^2 = ZnI^2 + Sn(CH^3)^4.$$
$$2Sn(CH^3)^3I + Zn(CH^3)^2 = ZnI^2 + 2Sn(CH^3)^4.$$

Also, together with metallic tin, by the distillation of stannous methide: $2Sn(CH^3)^2 = Sn(CH^3)^4 + Sn$.

It is a liquid having an ethereal odour, and boiling at 140°—145°. Iodine converts it into methylic iodide and stannic iodotrimethide.

By the action of zinc-ethyl on stannic iodomethides, and of zinc-methyl on stannic iodo-ethides, stannic compounds are produced, containing both ethyl and methyl, viz.:

$$2Sn(CH^3)^3I + Zn(C^2H^5)^2 = ZnI^2 + 2Sn(C^2H^5)(CH^3)^3.$$
$$Sn(C^2H^5)^2I^2 + Zn(CH^3)^2 = ZnI^2 + Sn(C^2H^5)^2(CH^3)^2.$$
$$2Sn(C^2H^5)^3I + Zn(CH^3)^2 = ZnI^2 + 2Sn(C^2H^5)^3(CH^3).$$

Stannic Ethotrimethide, $Sn(C^2H^5)(CH^3)^3$, is prepared by gradually adding stannic iodotrimethide to zinc-ethyl in a vessel cooled by immersion in cold water, the zinc-ethyl being kept in excess. On distilling the product, and mixing the distillate with water containing a little acetic acid, stannic ethotrimethide separates as a heavy oil, which is to be washed, dried with chloride of calcium, and rectified. It is a colourless liquid, of specific gravity 1·243, and boiling between 123° and 128°. Vapour-density, obs. (at 200°) = 6·715; calc. = 6·65. It has an ethereal, somewhat pungent odour. With iodine it forms ethylic iodide and stannic iodotrimethide (Cahours):

$$Sn(C^2H^5)(CH^3)^3 + I^2 = C^2H^5I + Sn(CH^3)^3I.$$

Stannic Diethodimethide, $Sn(C^2H^5)^2(CH^3)^2$, is obtained by gradually adding stannic di-iododiethide to an ethereal solution of zinc-methyl, keeping the latter in excess, and proceeding as in the preparation of the last-described compound.

It is a clear colourless liquid, having a faint ethereal odour, and metallic taste. Specific gravity = 1·232 at 19°. It remains fluid at −13°, and boils between 144° and 146°. Vapour-density, obs. (at 199°) = 6·838; calc. = 7·138. It is easily set on fire, and is decomposed by chlorine, bromine, and iodine, which take from it 1 at. methyl.

Iodine dissolves in the liquid with carmine-red colour, which disappears slowly in the cold, more quickly on application of heat. On adding an excess of iodine, removing this excess after a while by means of metallic mercury, and distilling, methylic iodide passes over first; the boiling-point then quickly rises to 207°, at which temperature very little passes over; and there remains a straw-coloured, somewhat oily, intolerably pungent liquid, having a specific gravity of 2·033 at 15°, and the composition of stannosostannic iododiethide, $Sn'''(C^2H^5)^2I$. It remains liquid at −13°, and begins to boil at 208°; but the temperature quickly rises, and at 230°, an abundant separation of iodide of tin takes places. The liquid is, perhaps, a mixture of stannic di-iododiethide, $Sn(C^2H^5)^2I^2$, and stannous ethide, $Sn(C^2H^5)^2$. (Frankland.)

Stannic diethodimethide, treated with aqueous hydrochloric acid, gives off a mixture of ethylic and methylic hydrides (more than four times as much of the former as of the latter), and is converted into a crystalline salt, probably a mixture of stannic dichlorodiethide and stannic dichlorodimethide. (Frankland.)

Stannic Triethomethide, $Sn(C^2H^5)^3(CH^3)$, is produced by the action of stannic iodotriethide on zinc-methyl, and separates, on treating the distillate with acidulated water, as a heavy oil, which may be purified as above. It is a colourless liquid, having an ethereal odour, boiling at 162°—163°, and is converted by iodine into methylic iodide and stannic iodotriethide. (**Cahours.**)

γ. AMYL-COMPOUNDS: STANNAMYLS.

These compounds, investigated, under Löwig's direction, by A. **Grimm** (Ann. Ch. Pharm. xcii. 383; Jahresb. 1854, p. 543), are produced by the action of amylic iodide on an alloy of 1 pt. sodium and 6 pts. tin, the process being conducted as in Löwig's method of preparing the stannethyls (p. 826). The distilled product contains the compounds $Sn''(C^5H^{11})^2$, $[Sn'''(C^5H^{11})^3]^2$, and $Sn^{iv}(C^5H^{11})^4$, homologous with the stannethyls, and, according to **Grimm**, also a compound containing $Sn^2(C^5H^{11})^2$.

The stannamyls are unctuous masses, insoluble in water, easily soluble in ether, and more soluble in alcohol in proportion as they contain less tin. They have not a very pungent odour, and do not fume in the air. They reduce silver-solution, and are oxidised with great violence by nitric acid. Bromine also acts violently on them; and iodine, in alcoholic solution, attacks them with evolution of heat. Their ethereal solutions oxidise when evaporated in contact with the air. The oxides have an alkaline reaction, dissolve in acids, and are separated from the solution by ammonia. Neither the radicles nor their compounds can be volatilised without decomposition. According to **Grimm**, all the stannamyls above mentioned act as radicles, uniting with oxygen, chlorine, iodine, &c. With respect to stannic amylide, $Sn(C^2H^5)^4$, however, this statement is very improbable, inasmuch as the corresponding ethyl- and methyl-compounds react as saturated molecules, not as radicles. Altogether, the investigation of the stannamyls must be regarded as imperfect; they have not, indeed, been separated, one from the other, with sufficient accuracy to give any value to the special description their properties, or of those of their compounds.

TIROLITE. Syn. with TYROLITE.

TITANATES.
TITANIC ACID. } See TITANIUM (p. 844).

TITANIFEROUS IRON. See TITANATES OF IRON (p. 846).

TITANITE. Syn. with SPHENE (p. 398). **Hautefeuille** (Compt. rend. lix. 698; Jahresb. 1864, p. 216) has obtained crystals having the form and composition of sphene, by fusing in a platinum crucible a mixture of 3 pts. silica and 4 pts. titanic oxide covered with chloride of calcium. If a small quantity of manganous chloride be added to the mixture, crystals of **greenovite** are obtained. If the mixture, in the fused state, be exposed to an atmosphere of aqueous vapour and carbonic acid, or (better) of air saturated with aqueous vapour and hydrochloric acid, crystals of **perowskite**, $Ca''Ti''O^3$, are obtained. (See TITANATES, p. 845.)

TITANIUM. *Symbol*, Ti; *Atomic weight*, 50.—A metallic element discovered, in 1789, by **Gregor**, in the menaccanite (titaniferous ironsand) of Cornwall, and thence named, by **Kirwan**, *Menachin*. **Klaproth**, in 1795, discovered a new metal in rutile, which he called *Titanium*; but on subsequent investigation, in 1797, he found that this metal was identical with the menachin of Gregor. The name titanium has, however, been universally adopted. The preparation and properties of titanium and its compounds have been studied chiefly by **Berzelius**, **Wöhler**, and **H. Rose**.

Titanium is one of the rarer metals, and is never found in the metallic state. The most important titanium minerals are rutile, brookite, and anatase, which consist of titanic oxide, TiO^2, and the several varieties of titaniferous iron, consisting of ferrous titanate, sometimes alone, but more generally mixed with ferric or ferroso-ferric oxide. Titanium likewise occurs native, as titanate of calcium, in perowskite; as silico-titanate of calcium in sphene or titanite; and as titanate of cerium, yttrium, &c., together with tantalates and niobates, in æschynite, euxenite, polymignite, polycrase, and pyrochlore. Small quantities of titanium are found also in many iron-ores, and it has been detected by **Mazade** (Compt. rend. xxxiv. 952) in the mineral water of Negrac (Dép. d'Arêche) in France.

When titaniferous iron-ores are smelted in the blast-furnace, small cubic crystals of a bright copper-colour are found on the slag which adheres to the lower part of the furnace. These crystals were long supposed to be metallic titanium, but **Wöhler** (Ann. Ch. Pharm. lxxiii. 34) has shown that they also contain carbon and nitrogen,—being, in fact, a compound of cyanide of titanium with nitride of titanium, $TiCy^2.3N^2Ti^3$.

Pure titanium is obtained by heating the double fluoride of potassium and titanium with potassium in a covered crucible. The metal is then set free, with vivid incandescence, and the fluoride of potassium may be removed by washing with water. Titanium thus obtained is a dark-green, heavy, amorphous powder, which does not exhibit any shade of copper-colour, even after pressure; under the microscope it appears as a cemented mass, having the colour and lustre of iron. Metallic titanium is also obtained by mixing titanic oxide with one-sixth of its weight of charcoal, and exposing it to the strongest heat of an air-furnace. It was thus obtained, in the form of a copper-coloured or gold-coloured powder, by Vauquelin, Lampadius, and others; but possibly the charcoal which they used may have contained nitrogen, and that element may have united with the reduced metal.

Pure titanium (prepared from the double fluoride) burns with great splendour when heated in the air, and, if sprinkled into a flame, is consumed, with brilliant scintillations, at a considerable distance above the point of the flame. When heated to redness in oxygen-gas, it burns with a splendour resembling a discharge of electricity. In chlorine-gas it exhibits similar phenomena, requiring also the aid of heat to set it on fire. Mixed with red lead and heated, it burns with such violence that the mass is thrown out of the vessel with loud detonation. Titanium does not decompose water at ordinary temperatures, but on heating the water to the boiling-point, hydrogen begins to escape. Warm hydrochloric acid dissolves titanium, with brisk evolution of hydrogen. Ammonia added to the solution throws down a black oxide; and on heating the liquid, hydrogen is evolved; and the precipitate first turns blue, and is afterwards converted into white titanic acid.

Titanium, in its most important compounds, is tetratomic, titanic oxide being TiO^2, and the corresponding chloride, $TiCl^4$, analogous to the oxide and chloride of silicon; it also forms a sesquioxide, Ti^2O^3, and a corresponding trichloride, $TiCl^3$.

TITANIUM, ALLOYS OF. These alloys have not been much examined. A compound of titanium and aluminium, Al^6Ti, is obtained by exposing 10 pts. titanic oxide, 30 pts. cryolite, and 30 pts. of a mixture of equal weights of potassium- and sodium-chlorides, for an hour, to the heat of melting silver, and dissolving out the excess of aluminium from the resulting regulus with hydrochloric acid. It forms pinchbeck-brown, microscopic, quadratic laminæ, which, when heated in hydrochloric acid gas, are resolved into chloride of aluminium and chloride of titanium. (Wöhler and Michel, Ann. Ch. Pharm. cxiii. 248; cxv. 102; Jahresb. 1860, p. 129.)

Respecting the alloys of titanium and iron, see IRON, iii. 370.

TITANIUM, BROMIDE OF. Only one bromide of titanium is known, namely the tetrabromide, $TiBr^4$, which is obtained by passing bromine-vapour over an ignited mixture of charcoal and titanic oxide. It then distils over as a red liquid, which solidifies in the receiver to a crystalline mass. When freed from excess of bromine by redistillation with mercury, it forms an amber-yellow mass, having a beautiful crystalline structure and a density of 2·6, melting at 39°, and boiling at 230°. It quickly absorbs moisture, and in contact with water, is resolved into hydrobromic acid and titanic acid.

TITANIUM, CHLORIDES OF. Titanium forms two chlorides, $TiCl^3$ and $TiCl^4$.

The *Trichloride*, or *Titanous Chloride*, discovered by Ebelmen (Ann. Ch. Phys. [3], xx. 385), is produced by the action of hydrogen on the tetrachloride. To prepare it, pure and dry hydrogen-gas is passed into titanic chloride contained in a tubulated retort, by means of a delivery-tube dipping into the liquid. To the neck of the retort is adapted a tube of glass or porcelain (if of glass, it should be wrapped in copper-foil), which passes horizontally through a furnace, projecting considerably beyond it, and terminating in a tubulated receiver to collect the titanic chloride which passes undecomposed through the tube. As soon as the apparatus is completely filled with hydrogen, the tube is heated to redness, and the retort containing the titanic chloride is gently warmed. Titanous chloride is then produced, and condenses in the part of the tube which projects beyond the furnace, the process being finished as soon as all the titanic chloride is driven out of the retort. The projecting part of the tube is then to be gently warmed, while hydrogen is continually passed through it in order to drive all the undecomposed titanic chloride into the receiver, and the titanous chloride is then left to cool in the current of hydrogen.

Titanous chloride forms dark-violet scales, having a strong lustre. When heated in a porcelain dish in contact with the air, it gives off vapours of titanic chloride, and leaves titanic oxide. It deliquesces in the air at ordinary temperatures, and is gradually decomposed in the same manner. Titanous chloride dissolves in water, forming a violet-red solution, which gradually loses its colour, and deposits titanic acid. From the aqueous solution, alkalis and alkaline carbonates throw down dark-brown titanous hydrate; the same precipitate is formed by sulphide of ammonium; sulphuric acid produces no reaction. The solution of titanous chloride is an extremely powerful deoxidising agent, reducing the noble metals from their solutions, converting cupric and ferric salts into cuprous and ferrous salts respectively, and separating sulphur from ulphurous acid when heated therewith. (Ebelmen.)

A violet-red solution of titanous chloride is also produced by boiling or digesting a solution of titanic acid in hydrochloric acid with finely-divided silver. (v. Kobell.)

Tetrachloride of Titanium, or *Titanic Chloride*.—This compound is produced by heating titanium, or nitride of titanium, in chlorine-gas. It is prepared in the same manner as chloride of silicon—namely, by mixing finely-divided titanic oxide to a paste with oil and charcoal, heating the mixture in a covered crucible, and igniting the charred mass in a porcelain tube through which a current of chlorine is passed. The titanic chloride is collected in a cooled receiver, freed from excess of chlorine by agitation with copper or mercury, and then rectified. If native rutile has been used in the preparation, ferric chloride is likewise produced; but the titanic chloride is easily separated from it by decantation and redistillation.

Pure titanic chloride is a colourless, transparent, heavy liquid, having an acid pungent odour, and emitting white fumes on exposure to the air. It has a specific gravity of 1·7609 at 0°, does not solidify at $-25°$, and boils at 135°. Vapour-density, obs. $= 6·836$ (Dumas); calc. (2 vols.) $= 6·653$. When exposed to the air, it absorbs moisture, and gradually solidifies to hydrated titanic chloride, which dissolves in a larger quantity of water. According to Merz (Bull. Soc. Chim. 1867, i. 401) the product thus formed is an oxychloride, $TiCl^4.3TiO^2.16H^2O$ (nearly), which gives off part of its chlorine, as hydrochloric acid, when placed over quicklime, more when heated to 100°, and nearly all the remainder at 180°. On mixing the anhydrous chloride with water, combination takes place, attended with so great a rise of temperature that the mass is scattered about. To obtain a clear aqueous solution of the chloride, it must be added to cold water by small quantities, care being taken that the liquid does not become heated. On heating, and evaporating the aqueous solution, hydrochloric acid is evolved, and titanic acid is precipitated. Titanic chloride is not decomposed by potassium at its boiling-point; but when its vapour is passed over heated potassium or sodium, the titanium is reduced, with incandescence, and evolution of heat sufficient to melt the glass at the point where the reaction takes place. (H. Rose.)

Titanic chloride forms a number of compounds, analogous to those of stannic chloride:—

α. With Ammonia, $TiCl^4.4NH^3 = (N^4H^{12}Ti^{iv})Cl^4$ (Wöhler); $TiCl^4.6NH^3$ (Persoz).—Dry ammonia-gas, passed over titanic chloride, is rapidly absorbed, with great evolution of heat. The saturated compound is a brown-red powder (Rose), pale-yellow (Persoz), which quickly decomposes in contact with the air. When heated in ammonia-gas, it is converted into nitride of titanium (p. 841). By ignition in hydrogen, it yields a yellow compound. When heated by itself, in a glass tube, it first gives off ammonia, then chloride of ammonium and hydrochloric acid, leaves a residue of metallic titanium, and yields a yellowish-white sublimate, consisting of a double chloride of ammonium and titanium, containing $3NH^4Cl.TiCl^4$, or $6NH^4Cl.TiCl^4$, according to the mode of preparation. This double salt is soluble in water. (H. Rose.)

β. With Chloride of Cyanogen, $2TiCl^4.Cy^2Cl^2$.—Already described under CYANOGEN (ii. 280).

γ. With Hydrocyanic Acid, $TiCl^4.HCy$. (See ii. 220.)

δ. With Phosphoretted Hydrogen.—Titanic chloride absorbs dry phosphoretted hydrogen-gas, forming, when saturated, a brown solid body, which fumes in contact with the air. It is decomposed by water, hydrochloric acid, potash, ammonia, and their carbonates, giving off phosphoretted hydrogen with effervescence. Gaseous ammonia likewise expels the phosphoretted hydrogen at ordinary temperatures, converting the brown compound, for the most part, into the ammonio-tetrachloride above described. The brown compound, when heated in a close vessel, gives off a little hydrochloric acid and phosphoretted hydrogen, and yields a yellow sublimate, containing $3TiCl^4.2H^3P.2HCl$, which likewise gives off phosphoretted hydrogen when treated with water, acids, or alkalis. (H. Rose, Pogg. Ann. xlii. 527.)

ε. With Tetrachloride of Sulphur. (See p. 536 of this volume.)

ζ. With Chloride of Ammonium (see above).

TITANIUM, CYANIDES OF. See CYANIDES (ii. 273).

TITANIUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions*.—The oxides of titanium are not reduced to the metallic state when heated on charcoal before the blowpipe, a character by which titanium is distinguished from tin.

Titanic oxide mixed with borax, or (better) with phosphorus-salt, forms in the outer blowpipe-flame a colourless glass; but in the inner flame, a glass which is yellow while hot, but assumes a violet colour on cooling. The same character is exhibited by those salts of titanic acid whose bases do not themselves impart any colour to the bead. If the titanic oxide contains iron, the colour of the bead is brown-red or blood-red, instead of violet. Many titanates yield the violet colour only with phosphorus-salt, not with borax. The colour is produced more readily by heating the substance on charcoal than on platinum-wire. According to Riley (Chem. Soc. Qu. J. xii. 13; Jahresb. 1859, p. 678), the delicacy of the reaction is much increased by melting a little metallic zinc in the phosphorus-salt bead, a distinct coloration being then produced, as the zinc is burnt away, even with very minute quantities of titanium.

2. *Reactions in Solution.*—Titanic acid and the neutral titanates are insoluble in water, but dissolve in acids, especially in hydrochloric and sulphuric acids. From these solutions the titanic acid is precipitated by boiling, imperfectly from the hydrochloric, completely from the sulphuric solution.—*Caustic alkalis* and *alkaline carbonates* likewise throw down from these solutions a white gelatinous precipitate of titanic acid. In the hydrochloric solution, containing as little free acid as possible, *infusion of galls* produces an orange-coloured precipitate.—*Ferrocyanide of potassium* forms, in the same solution, a dark-brown precipitate.—Metallic *tin*, immersed in a solution of titanic acid in hydrochloric acid, eliminates hydrogen, assumes a violet-blue colour, and, if the solution is not too dilute, throws down a dark-violet precipitate (protoxide of titanium?), which gradually turns white by oxidation. The violet-blue solution, when diluted with water, assumes a rose-colour, which often remains unaltered for several days. This reaction serves for the detection of very small quantities of titanium. (v. Kobell.)

Titanous oxide dissolves in acids, forming violet solutions, in which *alkalis* and *alkaline carbonates* form a dark-brown precipitate of titanous hydrate, gradually changing, with evolution of hydrogen, into titanic acid.—*Carbonate of calcium* precipitates titanous oxide completely from its solutions.—*Sulphydric acid* produces no alteration; *sulphide of ammonium* throws down brown titanous hydrate. The solution of titanous salts act as powerful reducing agents, precipitating *gold*, *mercury*, and *silver* from their solutions in the metallic state. Titanous chloride throws down white cuprous chloride from the solution of a *cupric salt*, and reduces *ferric* to *ferrous salts*. (Ebelmen).

3. *Estimation and Separation.*—Titanium is always estimated in the form of titanic oxide, TiO^2. This compound is best precipitated from its solutions in acids by ammonia, which throws it down in the form of a very bulky hydrate (titanic acid) resembling hydrate of alumina. A great excess of ammonia must be avoided, as it would redissolve a small portion of the titanic acid. The precipitate, after ignition, contains 60 per cent. of titanium.

If the titanic acid, after precipitation by ammonia, is to be redissolved in acids, which is sometimes necessary in order to separate it from other metals, great care must be taken in the precipitation to avoid all rise of temperature; and the precipitate must be washed with cold water, because heat has the effect of rendering titanic acid more or less insoluble in acids (p. 844).

Titanic acid may also, in some cases, be separated from its acid solutions by boiling; from the solution in sulphuric acid, complete precipitation is effected by this method; but when hydrochloric acid is the solvent, a small portion of titanic acid always remains in solution after boiling.

Titanic oxide (rutile, &c.) and its insoluble compounds are most easily rendered soluble by fusion with acid sulphate of potassium. The best mode of proceeding is to fuse in a platinum-crucible a quantity of the acid sulphate equal to about six times the weight of the titanate, add the mineral in extremely fine powder to this cooled mass, and fuse again till the whole flows quietly, and the powder is completely dissolved. The fused mass is then dissolved in a large quantity of cold water, and the solution precipitated by boiling.

Sesquioxide of titanium is precipitated from its solutions by ammonia, and the precipitate, after standing from 24 to 36 hours, is converted, with evolution of hydrogen, into titanic acid, in which form it may be estimated.

From the alkalis and alkaline earths, titanic acid may be separated by *ammonia*, the solution, in the latter case, being carefully excluded from the air. Baryta and strontia may also be separated by sulphuric acid.

Titanic acid is separated from magnesia by boiling, if the two are dissolved in sulphuric acid; and by precipitation with *carbonate of barium*, when hydrochloric acid is the solvent.

The separation from alumina, glucina, yttria, and thorina is also effected by boiling the sulphuric acid solution.

From zirconia, titanic acid may be separated by mixing the nearly neutralised solution with *hyposulphite of sodium*, and boiling till no more sulphurous anhydride is given off. The titanic acid is then completely precipitated, while the zirconia resolution.

From cerium and the allied metals, titanium is separated by precipitating the former with sulphate of potassium.

From the metals which are precipitated as sulphides by sulphide of ammonium—viz., manganese, iron, cobalt, nickel, uranium, and zinc—titanium is separated by mixing the acid solution with tartaric acid and excess of ammonia (which then forms no precipitate), and adding *sulphide of ammonium*, which precipitates everything but the titanium. The filtered solution is then evaporated to dryness, and the residue ignited in a platinum-crucible to expel ammoniacal salts, and burn away the carbon of the tartaric acid. As this carbonaceous matter is very difficult to burn, the ignition should either be performed in a muffle-furnace, or a stream of oxygen should be very gently directed into the crucible. The residue consists of titanic oxide, which may then be weighed.

The separation of titanium from iron may also be effected by precipitation with *hyposulphite of sodium*, the process being conducted exactly in the same manner as in separating aluminium from iron (i. 155).—For Riley's method of estimating titanium in pig-iron, see IRON, CARBURETTED (iii. 375).

From molybdenum, tungsten, and vanadium, titanium may be separated by means of sulphide of ammonium, which dissolves those metals as sulphides, and precipitates the titanium as titanic acid.

From bismuth, cadmium, copper, lead, tin, &c., titanium is easily separated by sulphydric acid.

Titanium may also be separated from tin, by fusing a mixture of stannic and titanic oxides with *sulphur* and *carbonate of sodium*. On treating the fused mass with water, the whole of the tin dissolves as sulphostannate of sodium, while the titanic acid remains undissolved, together with a small quantity of sodic titanate, which may be decomposed by ignition with sal-ammoniac; the chloride of sodium thereby formed may be dissolved out by water, leaving pure titanic acid.

From silicon.—When silicates containing small quantities of titanic acid are decomposed, in the usual way, by treatment with acids, or by fusion with an alkaline carbonate, the silica separated by evaporation, &c., and the alumina, ferrous oxide, and manganous oxide precipitated by ammonia, the greater part of the titanic acid will be found in this precipitate, while the smaller portion remains with the silica. The latter is treated with hydrofluoric and sulphuric acids, and the residue, consisting of titanic oxide, is mixed with the previously ignited precipitate of alumina, &c. This mixture is then fused with twice its weight of acid sulphate of potassium till the excess of sulphuric acid is for the most part volatilised, and the cooled mass is dissolved in water; whereby, if the operation has been well conducted, and the silica completely removed, a perfectly clear solution will be obtained. This solution is largely diluted, and sulphydric acid gas is passed through it, till the whole of the ferric oxide is reduced to ferrous oxide; and the solution, without previous filtration, is boiled for half an hour, while a stream of carbonic anhydride is continually passed through it (to prevent oxidation of the ferrous salt). The titanic acid is thereby completely precipitated, while all the other substances remain in solution. (Scheerer, Ann. Ch. Pharm. cxii. 178.)

In treating titaniferous silica with hydrofluoric acid to expel the silicon, the addition of sulphuric acid is indispensable, as otherwise a portion of the titanium will also be volatilised as fluoride. (Riley, Chem. Soc. Qu. J. xv. 311; Jahresb. 1862, p. 590.)

From tantalum and niobium, titanium is separated by fusing the mineral with acid sulphate of potassium, and treating the fused mass with cold water, which dissolves only the acid sulphate of titanium (iv. 51; v. 664).

Volumetric Estimation.—A method of estimating titanium volumetrically is founded on the reducibility of titanic oxide to titanous oxide by zinc in an acid solution, and the oxidability of the latter by permanganate of potassium. The titanic acid is dissolved in hydrochloric acid (if sulphuric acid is present, the titanic acid must first be precipitated by ammonia and then redissolved), the solution warmed with metallic zinc (in a flask provided with a vertical tube, so as to exclude the air as much as possible), till the colour of the liquid no longer increases in depth; and the solution, after dilution with de-aërated water, is mixed with permanganate of potassium, till the rose-red colour of the latter becomes manifest. Each atom of iron corresponding to the permanganate gives 1 at. titanium. (F. Pisani, Compt. rend. lix. 208; Jahresb. 1864, p. 705.)

A mixture of titanic oxide and zirconia is first rendered soluble by fusion with acid sulphate of potassium; the titanic acid is then determined as above, and the zirconia by difference.

Ferric oxide is reduced by zinc before titanic acid, and ferrous oxide is oxidised by the permanganate after it. To estimate iron and titanium together, the permanganate red, instead of violet. Many titanates yield the violet colour only with phosphorus-salt, not with borax. The colour is produced more readily by heating the substance on charcoal than on platinum-wire. According to **Riley** (Chem. Soc. Qu. J. xii. 13; Jahresb. 1859, p. 678), the delicacy of the reaction is much increased by melting a little metallic zinc in the phosphorus-salt bead, a distinct coloration being then produced, as the zinc is burnt away, even with very minute quantities of titanium.

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Ferric oxide is reduced by zinc before titanic acid, and ferrous oxide is oxidised by the permanganate after it. To estimate iron and titanium together, the permanganate is added till the violet colour disappears, and a drop of the liquid begins to be coloured, by sulphocyanate of potassium. The quantity of permanganate required for this purpose gives the titanic acid, and by further addition the iron may be determined. Or the ferric oxide may be reduced by sulphurous or sulphydric acid (neither of which acts upon titanic acid), and volumetrically determined by itself. In a mixture of titanic acid, zirconia, and ferric oxide, the first and third are determined as just described, and the zirconia by difference. (Pisani.)

4. *Atomic Weight of Titanium.*—H. Rose, in 1829 (Pogg. Ann. xv. 145), determined the atomic weight of this metal by decomposing a weighed quantity of titanic chloride, $TiCl^4$, with water, precipitating the titanic acid with ammonia, and estimating the amount of chlorine in the filtrate with nitrate of silver. In four experiments, 100 pts. titanic chloride yielded, as a mean, 301·7 pts. silver-chloride; whence (for $Ag = 108$, and $Cl = 35·5$) the atomic weight of titanium was found to be $= 48·26$.

An essentially similar method was followed by Pierre in 1867 (Ann. Ch. Phys. [3], xx. 257), who, however, made use of a titrated silver-solution, instead of weighing the chloride of silver. In five experiments, each made with from 700 to 800 milligrammes of titanic chloride, he found that 100 pts. of that compound required to precipitate the chlorine contained in them from 224·58 to 225·53 pts. silver. Hence Ti falls between 49·50 and 50·38, and, as a mean result of the five experiments, $Ti = 50·10$. The whole number, 50, is now generally adopted.

TITANIUM, FLUORIDE OF. *Titanous Fluoride*, TiF^3, is obtained (though impure) as a violet powder, by igniting potassio-titanic fluoride (*infra*) in a stream of hydrogen-gas, and treating the resulting mass with hot water. (R. Weber, Pogg. Ann. cxx. 287; Jahresb. 1863, p. 211.)

Titanic Fluoride, TiF^4, is obtained by distilling a mixture of fluor-spar and titanic oxide with fuming sulphuric acid in a platinum apparatus; it then passes over as a fuming colourless liquid (Underdorben). By dissolving titanic acid in hydrofluoric acid, and evaporating, a syrupy liquid is obtained, which deposits crystals of titanic fluoride. These crystals are resolved by water into soluble hydrotitanic fluoride, and insoluble titanic oxyfluoride.

Hydrotitanic Fluoride, $H^2TiF^6 = 2HF.TiF^4$, is produced, as just stated, in the decomposition of titanic fluoride by water; also by dissolving titanic oxide in aqueous hydrofluoric acid (Berzelius). It is an acid, and, when neutralised with bases, yields double salts of titanic fluoride, represented by the general formula, $2MF.TiF^4$.

Ammonio-titanic Fluoride, $2NH^4F.TiF^4$, is produced by adding ammonia to aqueous hydrotitanic fluoride, till the precipitated titanic acid no longer redissolves. On evaporating the liquid, it separates in shining scales, which, when heated in a platinum apparatus, yield, much below a red heat, a sublimate of ammonium-fluoride, leaving a residue probably consisting of $NH^4F.TiF^4$. (Berzelius.)

Calcio-titanic Fluoride forms prismatic crystals, which dissolve without decomposition in acidulated water, but are decomposed by pure water, with separation of a white powder.—*Cupro-titanic fluoride*, obtained by mixing the solutions of the component fluorides, crystallises in long, pale, blue-green needles, soluble without decomposition in acidulated water.—The *ferric salt*, $2FeF^3.TiF^4$, is produced by mixing the solutions of the component salts. The yellow solution leaves, on spontaneous evaporation, a yellow syrup, and when gently heated, a pale-yellow crystalline mass, soluble in water without decomposition.—The *magnesium-salt*, prepared in like manner, separates by spontaneous evaporation in long needles, which have a bitter taste, are decomposed by pure water, but dissolves without decomposition in acidulated water.—The *lead-salt*, prepared in like manner, forms small colourless crystals, which have a sweet and afterwards an astringent taste, and dissolve readily in water without decomposition (Berzelius).—The *nickel-salt*, $NiF^2.TiF^4.6H^2O$, is produced by dissolving titanic acid and nickel-oxide in hydrofluoric acid, and separates in green, easily soluble crystals. (Weber.)

The *potassium-salt*, $2KF.TiF^4$, prepared like the ammonium-salt, crystallises in scales, which, when dry, are milk-white, and have a silky lustre (Berzelius).—Wöhler prepares it by fusing very finely-pounded rutile in a platinum-crucible with twice its weight of potassic carbonate, and dissolving the fused and pulverised mass in a platinum-dish, in the requisite quantity of dilute hydrofluoric acid. The double fluoride then partly crystallises out, and on heating the liquid to the boiling-point, adding water if necessary till the salt is redissolved, and filtering hot, the greater part separates in shining scales, so that the entire liquid solidifies to a pulp. The salt is to be washed on a filter with cold water, pressed between filter-paper, and crystallised from boiling water. It forms nacreous scales when dry, and melts without decomposition at a white heat.

The *sodium-salt* forms indistinctly crystalline crusts, more soluble than the potassium-salt. (Berzelius.)

TITANIUM, IODIDE OF. TiI^4. (R. Weber, Pogg. Ann. lxx. 287.—Hautefeuille, Bull. Soc. Chem. 1867, i. 201.)—Produced: 1. By passing iodine-vapour over ignited titanium (Weber).—2. By passing dry hydriodic acid·gas into titanic chloride gradually heated to its boiling-point, and maintained at that temperature till the transformation is complete: the small quantity of free iodine which gives the product a violet tinge may be removed by three or four distillations in a stream of hydrogen (Hautefeuille).—3. By passing the vapour of titanic chloride, mixed with hydrogen and iodine-vapour, through a tube heated to dull redness. The iodide, which is not very volatile, then condenses in the cold part of the tube, mixed, however, with a large quantity of free iodine, which renders it more difficult to purify than that obtained by the second method. (Hautefeuille.)

Titanic iodide forms a brittle mass, having a reddish-brown colour and metallic lustre. It melts to a brown liquid at 150°, remains in a state of surfusion till cooled somewhat below 100°, and crystallises on further cooling, in bulky octahedrons, which change, in a few days, to tufts of silky prismatic crystals. It has a sensible vapour-tension at ordinary temperatures, and fumes strongly in the air. It boils at a little above 360°, and distils without decomposition. Vapour-density, obs. (at 440°) = 18·054; calc. = 19·334. The lower density found by observation indicates an increased coefficient of expansion at high temperatures, perhaps arising from dissociation. The superheated vapour burns, in contact with the air, with a very bright flame, yielding iodic and titanic oxides.

Titanic iodide dissolves rapidly in water, but with less rise of temperature than the chloride. The aqueous solution, when exposed to the air, turns brown, and yields titanic acid.

TITANIUM, NITRIDES OF. By heating the ammonio-chloride of titanium, $4NH^3.TiCl^4$, by itself (H. Rose), or better in a stream of ammonia-gas (Liebig), a copper-coloured substance is obtained, which was originally supposed to be metallic titanium, but which Wöhler has shown to consist of nitride of titanium, Ti^3N^4, or more probably $Ti^6N^8 = 3TiN^2.Ti^3N^2$; it contains 28 per cent. of nitrogen. This compound is redder than the cubic crystals of the blast-furnaces, which have a tinge of yellow. Another nitride of titanium, TiN^2, is produced when titanic oxide is strongly heated in a stream of ammoniacal gas. Its powder is dark-violet, with a tinge of copper-colour; in small pieces it exhibits a violet copper-colour and metallic lustre. A third nitride, Ti^5N^6, or more probably $2TiN^2.Ti^3N^2$, is formed when Rose's titanium is subjected to the action of a stream of hydrogen at a strong red heat. It has a brassy or almost golden-yellow colour and metallic lustre. It is also obtained (mixed, however, with carbon) when titanic oxide is heated to redness in a stream of cyanogen-gas or hydrocyanic acid vapour; no cyanide of titanium is formed in this reaction. All these three nitrides of titanium sustain, without decomposition, a temperature at least equal to that of melting silver. Mixed in the state of powder with the oxides of copper, lead, or mercury, and heated, they emit a lively sparkling flame, and reduce the oxides to the metallic state. When fused with hydrate of potassium, they give off ammonia-gas. (Wöhler, Ann. Ch. Pharm. lxxiii. 34; Jahresb. 1849, p. 267.)

Wöhler and Deville (Ann. Ch. Pharm. ciii. 230; cv. 108; Jahresb. 1857, p. 174), by heating fluoride of titanium and potassium or sodium in an atmosphere of nitrogen, and boiling out the cooled mass with hydrochloric acid, obtained a nitride of titanium in the form of a dark-brown powder, composed of brass-yellow laminæ and prisms. When titanic chloride is passed through a strongly-ignited glass tube, in the fore part of which lumps of sal-ammoniac are placed, so that this salt may be volatilised with the titanic chloride, hydrochloric acid and nitride of titanium are immediately formed (the nitrogen being derived from the air), the latter coating the inside of the tube with a copper-coloured deposit. Nitride of titanium is also formed by heating a mixture of fluoride of titanium and potassium, chloride of sodium, and chloride of potassium, with aluminium; or by heating a mixture of titanic chloride and hydrogen-gas with aluminium, in presence of nitrogen.

TITANIUM, NITROCYANIDE OF. $TiCy^2.3Ti^3N^2$.—This is the copper-coloured compound already spoken of as occurring in iron-smelting furnaces, and formerly mistaken for metallic titanium. (See CYANIDES, ii. 273.)

TITANIUM, OXIDES OF. Two oxides of titanium are known with certainty, viz. Ti^2O^3, and TiO^2; the existence of a lower oxide, TiO, is likewise probable.

Protoxide of Titanium, TiO?—This oxide appears to be formed when titanic oxide is exposed, in a charcoal-lined crucible, to the highest heat of an air-furnace. Where the oxide is in contact with the charcoal, a thin coating of metallic titanium is formed; but within it is changed to a black mass, which is insoluble in all acids, is not otherwise affected by them, and is oxidised with difficulty when heated in contact with the air, or fused with nitre. The same oxide appears to be formed, in the wet way, as a dark-purple powder, when a fragment of zinc or iron is introduced into a solution of titanic acid in hydrochloric acid; but it alters very quickly by absorption of oxygen, so that there is considerable difficulty in studying its properties; the composition assigned to it is therefore hypothetical. The blue powder is, perhaps, a compound of titanium-protoxide with oxide of zinc or iron.

Sesquioxide of Titanium, or **Titanous Oxide,** Ti^2O^3.—This oxide is obtained, by passing dry hydrogen-gas over ignited titanic oxide, as a black powder, which, when heated in the air to a very high temperature, oxidises to titanic oxide. It is not attacked by nitric or hydrochloric acid; sulphuric acid dissolves it, forming a violet solution (Ebelmen).—A hydrate of titanous oxide, or titanous hydrate, is formed (according to Fuchs) by digesting a solution of titanic acid in hydrochloric acid at 40° or 50° with metallic copper, and pouring the resulting violet-blue solution into aqueous ammonia: it then falls down as a dark-brown precipitate, while cuprous chloride remains in solution. Instead of copper, silver reduced by zinc may be used in the preparation (v. Kobell). The hydrate is likewise formed (according to Ebelmen) when a solution of titanous chloride is precipitated by alkalis. The dark-brown precipitate thereby formed gradually turns black, blue, and finally white, while hydrogen is evolved. The blue colour is, perhaps, due to the formation of a titanous titanate.

Titanous oxide dissolves in *acids*, forming violet solutions; but the sulphate is the only titanous oxysalt that has been obtained in the solid state (see SULPHATES, p. 616). Titanous chloride has been already described. The solutions of titanous salts are powerful reducing agents, and yield a brown precipitate of titanous hydrate with alkalis (p. 838).

Dioxide of Titanium, Titanic Oxide or **Anhydride,** TiO^2. *Anhydrous Titanic acid.*—This oxide occurs native in three different forms: viz., as rutile and anatase, which are dimetric, and as brookite, which is trimetric. Rutile, which is the most common form of titanic oxide, occurs in acuminated dimetric prisms, isomorphous with tinstone, and exhibiting the combination P . ∞P . P∞ . ∞P∞ (*fig.* 322, ii. 160), also without P∞. For P, the length of the principal axis is 0·6442. Angle P : P = 123° 8′ in the terminal, and 84° 40′ in the lateral edges. Twin crystals occur, formed in the same manner as those of stannic oxide (p. 815). The crystals cleave distinctly parallel to ∞P and ∞P∞. Hardness = 6 to 6·5. Specific gravity = 4·18 to 4·25. Lustre, metallic adamantine. Colour reddish-brown, passing into red; sometimes yellowish, also black. Streak pale-brown. Subtransparent to opaque. Fracture subconchoïdal, uneven. Brittle.

Rutile occurs in granite, gneiss, mica-slate, and syenitic rocks; sometimes in granular limestone; generally in imbedded crystals. It is found in Brazil, at Arendal in Norway, on the Saualp in Carinthia, in the Urals, in the Tyrol, on the St. Gothard, at Yrieix in France, at Krumhennersdorff near Freiberg, in Castile, at Ohlapian in Transylvania, at Cairngorm in Scotland, at Craig Cailleach near Killin, and in Benzloe in the isle of Murray, Shetland; also at numerous localities in North America. It always contains from 1½ to 2½ per cent. ferric oxide, and sometimes stannic and tungstic oxides. A variety from Karingsbricka, in Sweden, contains a small percentage of chromium, and is the *titane oxydé chromifère* of Hauy.

Anatase, the purest form of native titanic oxide, is also dimetric; but its form is incompatible with that of rutile, from which it also differs in its mode of cleavage, specific gravity, hardness, and other physical characters. It usually occurs in very acute unmodified octahedrons, having the principal axis = 1·7723: and the angle P : P . in the terminal edges = 97° 55′, in the lateral edges = 136° 30′; sometimes also in a combination like *fig.* 222 (ii. 235). Respecting its physical characters, and the localities of its occurrence, see i. 289.

Brookite, or Arkansite, which consists of titanic oxide mixed with about 3 to 4½ per cent. ferric oxide, is trimetric, having the axes = 0·5941 : 1 : 0·5611. Angle P : P (brach.) = 135° 37′; P : P (macr.) = 101° 3′; P : P (basal) = 95° 22′; ∞P̄ : ∞P2 = 99° 50′. The crystals frequently exhibit the combination ∞P̆∞ . ∞P̄2 . P, like *fig.* 273 (ii. 148), together with other pyramids and horizontal prisms, and are generally flat between the predominant faces ∞P̆∞; often also of pyramidal character, exhibiting the faces P, ∞P̆2 equally developed, like *fig.* 272 without P̆∞. (Kopp's *Krystallographie*, 2te Aufl. p. 267). For the physical characters and the localities of brookite, see i. 680.

Preparation.—Pure titanic oxide may be prepared from rutile, or from the several varieties of titaniferous iron; in the latter case a considerable portion of the iron may be removed by repeatedly boiling the pulverised mineral with hydrochloric acid.

H. Rose fuses the very finely-divided mineral with 3 pts. potassic carbonate, and treats the fused potassic titanate thus obtained with cold water. The excess of alkali is thereby removed, together with silicate, manganate, and stannate of potassium; whilst acid titanate of potassium remains undissolved, together with ferric oxide, and perhaps a small quantity of stannic oxide. This residue is washed on a filter with cold water, till the wash-water begins to run through milky, and then dissolved in concentrated hydrochloric acid. To obtain pure titanic acid from this solution, Berthier dilutes it with a considerable quantity of water, passes sulphydric acid gas through it to precipitate any tin that may be present, and adds ammonia to the filtered liquid as long as any precipitate is thereby produced. This precipitate contains titanic acid contaminated with sulphide of iron, and perhaps, also, with sulphide of manganese. The liquid (which should smell strongly of ammonium-sulphide) is to be well shaken, and then left to clarify by subsidence; afterwards decanted, and the precipitate treated with concentrated aqueous sulphurous acid, which completely dissolves the sulphides of iron and manganese, but leaves the titanic acid undissolved; the latter may then be collected on a filter, and washed. The solution in hydrochloric acid may also be boiled with sulphite of ammonium as long as the resulting precipitate continues to increase; this precipitate then consists of pure titanic acid, the whole of the iron remaining in solution as ferrous salt. The precipitate must be washed on a filter, out of contact with the air, to prevent the formation and precipitation of ferric oxide, and then ignited. (Berthier.)

Wöhler melts finely-pulverised rutile, in a platinum-crucible standing in an earthen crucible, with twice its weight of potassic carbonate, and dissolves the pulverised mass in dilute hydrofluoric acid, whereupon potassio-titanic fluoride separates in crystals. To dissolve this compound, the mass is heated to the boiling-point, with addition of water, if necessary, and the liquid is filtered as hot as possible. If excess of hydrofluoric acid be avoided, the solution may be effected in a glass vessel. The potassio-titanic fluoride, which separates in shining crystalline scales on cooling, is washed on a filter with cold water, and purified by recrystallisation from boiling water; its hot aqueous solution is mixed with ammonia, which throws down titanate of ammonium; and the salt, when ignited, gives off ammonia, and is converted, with incandescence, into pure titanic oxide. This process is also well adapted for preparing titanic oxide from titaniferous iron. The mass obtained by fusing this mineral with carbonate of potassium, is dissolved in dilute hydrofluoric acid, which leaves behind the greater part of the iron, in the form of ferric oxide. After the greater part of the potassio-titanic fluoride has crystallised out, and been purified as above, the ferruginous mother-liquors are treated with chlorine-water, or an alkaline hypochlorite, to bring the iron to its highest stage of oxidation, and then treated in the cold with dilute ammonia, which precipitates all the ferric oxide, with only a small portion of titanic acid. This precipitate is quickly separated by filtration, and the liquid, when boiled, deposits titanate of ammonium, which may be converted, by ignition, into titanic oxide. (Wöhler, Ann. Ch. Pharm. lxxiv. 212.)

Merz (J. pr. Chem. xcix. 157; Bull. Soc. Chim. [1867], ii. 400) modifies Wöhler's process, by fusing rutile with four times its weight of potassic carbonate, digesting the fused mass in water, dissolving the residual acid titanate of potassium by the prolonged action of strong hydrochloric acid, and boiling the resulting solution in a leaden dish with fluoride of potassium. The liquid, on cooling, solidifies to a crystalline pulp of potassio-titanic fluoride, $2KF.TiF^4$, which may be purified by washing it with a little cold water, and precipitating traces of iron with a drop of ammonium-sulphide. It is then to be redissolved in boiling water, and the titanic acid precipitated by ammonia. Another method is to melt 1 pt. of rutile with 6 pts. acid sulphate of potassium, digest the fused mass in water, neutralise the liquid with soda, and heat it to the boiling-point, passing a stream of sulphydric acid gas through it, at the same time, to bring the iron to the state of ferrous salt. Titanic acid is then precipitated free from iron. (Merz.)

A very pure product is likewise obtained by decomposing titanic chloride (prepared by igniting a mixture of rutile and charcoal in chlorine-gas) with water or ammonia.

Anhydrous titanic oxide, obtained by ignition of the precipitated hydrate, forms reddish-brown lumps, which resemble rutile more nearly in lustre and colour, in proportion as they have been more strongly heated. It may be obtained in the crystalline form by passing the vapour of titanic chloride, mixed with steam, through a red-hot tube. According to Ebelmen (Compt. rend. xxxii. 330), it is obtained, in long needle-shaped crystals, by exposing the amorphous oxide, mixed with microcosmic salt, to a temperature somewhat below that of a porcelain furnace. According to Deville and Caron (*ibid.* xlvi. 704), titanic oxide crystallised in the form of rutile, may be obtained by decomposing a fusible titanate, especially stannous titanate, with silica at a high temperature. Deville finds also (Compt. rend. lii. 1864), that the amorphous oxide is converted into quadratic crystals (like rutile or anatase) by ignition in hydrochloric acid gas; the crystals are coloured blue, in consequence of the formation of a small quantity of a lower oxide. Hautefeuille (Compt. rend. lvii. 148; lx. 188; Jahresb. 1863, p. 212; 1864, p. 213) has also obtained crystallised titanic oxide by two methods: α. By decomposing titanic chloride or fluoride with aqueous vapour.—β. By crystallising amorphous titanic oxide in an atmosphere hydrochloric or hydrofluoric acid. The second method is, however, only a modification of the first, inasmuch as titanic chloride or fluoride is first formed, and subsequently decomposed. Under the influence of hydrochloric acid, the formation of crystallised titanic oxide takes place only at very high temperatures, and the crystals produced have always the form of rutile: under the influence of hydrofluoric acid, on the contrary, anatase is formed at the lowest red heat, brookite at a somewhat higher temperature, and rutile at very high temperatures.

Anhydrous titanic oxide melts only at the heat of the oxyhydrogen-blowpipe. It is completely insoluble in water, and in all acids excepting strong sulphuric acid. When heated in the pulverised state with this acid till the excess is driven off, the residue dissolves in water after cooling. By fusing the anhydrous oxide with six times its weight of acid potassic sulphate, a clear yellow mass is obtained, which dissolves perfectly in warm water, forming a clear solution.

Potassium and *sodium* reduce titanic oxide at a red heat, forming oxide of potassium or sodium, and a black mass, which does not acquire metallic lustre, and appears to be a mixture of metallic titanium with titanic or titanous oxide.—*Charcoal*, at white heat, reduces titanic oxide to the metallic state.—*Carbonic disulphide*, at a strong red heat, converts titanic oxide into sulphide of titanium, with simultaneous formation of carbonic oxide and carbonic dioxide (H. Rose).—When dry *chlorine-gas* is passed over an ignited mixture of titanic oxide and charcoal, titanic chloride is produced (p. 837). The oxide, fused with *alkaline carbonates*, yields titanates of alkali-metal.—*Ammonia-gas*, at a bright red heat, reduces titanic oxide to violet nitride of titanium, TiN^2 (Elsner.)

TITANIC HYDRATES OR ACIDS.—There appear to be two modifications of titanic acid, analogous in some respects to stannic and metastannic acid.—α. One of these, called titanic acid, is precipitated by ammonia from the solution of titanic chloride. It is a white powder, of specific gravity 3·8 to 3·93 according as it has been exposed to a higher or lower temperature. When heated, it assumes a transient yellow colour, becoming white again on cooling. Its conversion into titanic oxide, at a higher temperature, is attended with vivid incandescence.

Titanic hydrate dissolves easily in sulphuric, nitric, and hydrochloric acids, even when these acids are rather dilute; but these dilute solutions, when boiled, deposit metatitanic hydrate as a soft white powder, which, like anhydrous titanic oxide, is quite insoluble in all acids, excepting strong sulphuric acid. It also resembles the anhydrous oxide in not exhibiting incandescence when heated. Titanic hydrate, precipitated by ammonia, is also converted into insoluble metatitanic hydrate by washing with hot water, or drying at a high temperature.—According to R. Weber (Pogg. Ann. cxx. 287; Jahresb. 1863, p. 210), a recently prepared aqueous solution of titanic chloride is not clouded by sulphuric, nitric, or hydrochloric acid, but phosphoric, arsenic, and hydriodic acids give precipitates with it immediately, and acid potassic chromate after some time. If, however, the same solution be heated to the boiling-point for only a few seconds, it immediately yields, with hydrochloric, nitric, sulphuric, hydrofluoric, and even organic acids, a white precipitate of metatitanic hydrate, and with dichromate of potassium an immediate orange-yellow precipitate. The precipitated metatitanic hydrate dissolves completely in a large quantity of water, after the supernatant acid has been poured off, and is reprecipitated from the solution by acids. Metatitanic acid is also produced by oxidising metallic titanium with nitric acid of specific gravity 1·25. (Weber.)

Titanic hydrate dried over oil of vitriol, has, according to H. Rose, the composition, H^2TiO^3, or $H^2O.TiO^2$, but always contains a little ammonia which cannot be removed by washing. According to Merz (*loc. cit.*), titanic hydrate, after drying in the air for twenty-four hours, contains $H^2TiO^3.2H^2O$; after drying for several weeks, $H^2TiO^3.H^2O$. When dried over oil of vitriol, it quickly loses 1 at. water; and after being left for some time over oil of vitriol, or dried at 60°, it contains $3H^2TiO^3.TiO^2$, and finally, after drying at 100°, $H^2TiO^3.TiO^2$.

Metatitanic acid, deposited from its solution in sulphuric acid on boiling, contains, after prolonged drying in the air, or for twenty-four hours over oil of vitriol, H^2TiO^3; at 60°, it contains $H^2TiO^3.TiO^2$; at 100°, $H^2TiO^3.2TiO^2$; at 120°, $H^2TiO^3.3TiO^2$; at 160°, $H^2TiO^3\,4TiO^2$. In short, metatitanic acid gives up its water more easily than titanic acid. (Merz.)

When a solution of titanic hydrate in hydrochloric acid is subjected to dialysis, insoluble gelatinous titanic hydrate remains in the dialyser (Graham, Chem. Soc. J. xv. 256). A solution of gelatinous titanic hydrate in hydrochloric acid, prepared in the cold, and containing only 1 per cent. TiO^2, when left in the dialyser for some days, yields liquid titanic acid, which, when subjected to the action of alcohol and other liquids, form compounds analogous to those produced in like manner with silicic acid. (Graham, *ibid.* xvii. 325; Jahresb. 1864, p. 178.)

Titanic Salts.—Titanic hydrate acts as a weak base, and likewise as an acid, forming salts both with acids and with alkalis. The salts in which it plays the part of base are very unstable. The oxalate, phosphate, and sulphate have been partially studied by H. Rose (iv. 266, 584; v. 606); the sulphate, phosphate, and nitrate also by Merz (*loc. cit.*).

Nitrate.—Titanic hydrate dissolves in concentrated nitric acid, and the solution, evaporated over quicklime, first becomes covered with an iridescent film, and then yields a mass of shining laminæ, containing $5TiO^2.N^2O^5.6H^2O$, or $5H^2TiO^3.2HNO^3$.—This salt dissolves, though imperfectly, in cold water; the clear solution, heated to 100°, deposits titanic oxide. (Merz.)

Phosphate.—Phosphate of ammonium, added to a solution of titanic hydrate in hydrochloric acid, throws down nearly all the titanium in the form of a white gelatinous precipitate, which, when washed and dried, forms a porcelain-like mass, containing $2TiO^2.P^2O^5$. Merz is of opinion that the original precipitate contains $TiO^2.P^2O^5$, but that the phosphoric acid is partly removed by washing. (Merz.)

Sulphate.—The solution of titanic hydrate in sulphuric acid deposits the hydrate on dilution with water. Titanic hydrate, moistened with very strong sulphuric acid, becomes hot, and dissolves completely at the boiling heat. The solution gelatinises on cooling; but if part of the sulphuric acid is evaporated, there remains a white powder, which, when dried on a porous tile and then heated to 180°, contains $TiO^2.SO^3$ or $Ti^{iv}(SO^4)^2.TiO^2$. This salt gives up all its sulphuric acid at a red heat, or when treated with water. Hydrochloric acid dissolves it slowly in the cold, more easily when heated. (Merz.)

Titanates.—These salts have not been much studied. Most of them may be represented by the formulæ $M^4TiO^4 = 2M^2O.TiO^2$, and $M^2TiO^3 = M^2O.TiO^2$, analogous to the ortho- and meta-silicates. The titanates of calcium and iron occur as natural minerals. The titanates of the alkali-metals are formed by fusing titanic oxide with alkaline hydrates, carbonates, or acid sulphates—some of them also in the wet way. When finely pulverised and levigated, they dissolve in moderately warm, concentrated hydrochloric acid; but the greater part of the dissolved titanic acid is precipitated on boiling the solution with dilute acids. The neutral titanates of the alkali-metals, M^2TiO^3, are insoluble in water, but soluble in acids. The titanates of the earth-metals and heavy metals are insoluble, and may be obtained by precipitation. Hautefeuille has prepared several of them in crystals, the form and physical characters of which are, in some cases, identical with those of native titanates.

Titanate of Calcium, $CaTiO^3$.—This compound occurs native as *Perowskite*, in small cubes and other monometric forms, with cubic cleavage tolerably perfect. Hardness = 5·5. Specific gravity = 4·017. Lustre metallic adamantine, less bright on the cleavage-faces. Colour greyish to iron-black. Streak uncoloured to greyish. Opaque to subtranslucent.

Analyses:—*a.* From Achmatowsk, near Slatoust, in the Ural: black (Jacobson, Pogg. Ann. lxii. 596).—*b.* From the same: brown (Brooks, *ibid.*).—*c.* From the Findelen Glacier, near Zermatt (Damour, Ann. Min. [4], vi. 313).—*d.* From Vogtsburg on the Kaiserstuhl (Seneca, Ann. Ch. Pharm. civ. 371):

	a.	*b.*	*c.*	*d.*
Titanic oxide	58·96	59·00	59·23	59·12
Lime	39·20	36·76	39·92	35 81
Magnesia	. . .	0·11		
Ferrous oxide	2·06	4·79	1·14	6·11
	100·22	100·66	100·29	101·04

Sphene (or titanite) is a silico-titanate of calcium, $CaSiO^3.CaTiO^3$ (p. 398). Respecting the artificial crystallisation of this compound and of calcic titanate, see TITANITE (p. 835). The artificial crystals of calcic titanate are said by Hautefeuille to be dimetric, whereas those of natural perowskite are monometric.

Titanates of Iron.—*a. Ferric titanate* is prepared by igniting finely-pulverised titaniferous iron (p. 846) with several times its weight of calcium-chloride, treating the fused mass with water to remove calcium-chloride and ferric chloride, and the residue with concentrated hydrochloric acid, which dissolves titanate of calcium. Ferric titanate then remains in long, thin, opaque needles, having a dark steel-grey colour and brilliant lustre. The crystals dissolve in melting acid potassic sulphate, forming a yellow liquid, which dissolves in water when cold; they are not altered by ignition in contact with the air, or in chlorine-gas, or by boiling with strong hydrochloric or sulphuric acid. (Liebig and Wöhler.)

β. Ferrous titanate, Fe^2TiO^4 or $2FeO.TiO^2$, is produced by fusing a mixture of 2 pts. titanic oxide, 5 pts. ferrous fluoride, and a large excess of sodium-chloride. On treating the fused product with a large quantity of water, removing the lighter substances by levigation, and heating the residue with dilute acetic acid till all laminar products are dissolved out, ferrous titanate remains in small prismatic crystals, having a dark-purple colour and the lustre of steel, and yielding an ochre-yellow powder. Their specific gravity is 4·37; they are not magnetic, and do not contain any ferric oxide. (Hautefeuille, Jahresb. 1864, p. 218.)

γ. The mineral called *Titaniferous Iron*, or *Ilmenite*—also, in certain varieties, *Crichtonite*, *Menakan*, *Menaccanite*, *Kibdelophane*, *Basanomelane*, *Hystatite*, *Washingtonite*, *Mohsite* — consists, sometimes of nearly pure ferrous titanate, sometimes of magnesio-ferrous titanate, sometimes of isomorphous mixtures of ferrous titanate with ferric oxide and ferroso-ferric oxide. It occurs in hemihedral, rhombohedral crystals (tetartohedral to the hexagonal type), isomorphous with iron-glance, having the principal axis = 1·3767, the angle R : R in the terminal edges = 85° 43′, and cleaving imperfectly parallel to R and oR; where the cleavage appears to be perfect, it is probable that combination-faces of different individuals exist (Kopp's *Krystallographie*, p. 211). The crystals are more or less tabular, often forming twins, united by the face R or oR; also implanted or imbedded, and united into groups, with scaly or granular structure. The mineral likewise occurs compact, in massive or in loose grains, and in the form of sand (titaniferous sand, titaniferous ironsand). Hardness = 5·0 to 6·0. Specific gravity = 4·6 to 5·0. Lustre submetallic. Colour iron-black to steel-grey. Streak black to brownish-red. Opaque. Fracture conchoïdal. Slightly magnetic. Before the blowpipe it is infusible, or becomes rounded in the reduction-flame at the edges only (the variety from Uddewalla, in Sweden, is fusible, according to Plantamour). With fluxes it gives the reactions of iron; the microcosmic salt bead becomes red or brown-red in the inner flame, and violet when treated with tin upon charcoal; many varieties give the manganese reaction with soda and nitre. The finely-pulverised mineral dissolves with more or less facility in hydrochloric acid, leaving a residue of titanic acid. The solution is generally yellow, containing both ferric and ferrous oxides. When heated with strong sulphuric acid, it acquires a dark-blue colour, which however disappears on addition of water, titanic acid then remaining undissolved.

Analyses:—A. *Containing little or no Ferric Oxide*.—*a*. From St. Christophe, near Bourg d'Oisans, in Dauphine: *Crichtonite*; specific gravity = 4·727 (Marignac, Ann. Ch. Phys. [3], xiv. 50).—*b*. Ingelsberg, near Hofgastein, in the Pinzgau: *Axotomous Iron-ore; Kibdelophane*: crystallised; non-magnetic, or very slightly magnetic; α. Specific gravity = 4·661 (v. Kobell, Schw. J. lxiv. 59, 245); β. Specific gravity = 4·689 (Rammelsberg, *Mineralchemie*, p. 408).—*c*. Rio Chico, province of Antioquia, New Granada: grains from the auriferous and platiniferous sand (Damour, Ann. Min. [3], li. 445).—*d*. Layton's Farm in the State of New York: crystallised, yielding a brown-black powder; non-magnetic; specific gravity = 1·293—4·313 (Rammelsberg):

	a.	*b*.		*c*.	*d*.
		α.	β.		
Titanic oxide	52·27	59·00	53·03	57·09	57·71
Ferric oxide	1·20	4·25	2·66		
Ferrous oxide	46·53	36·00	38·30	42·12	26·82
Manganous oxide	. .	1·65	4·30	0·80	0·90
Magnesia	. .	. .	1·65	. .	13·71
	100·00	100·90	99·94	100·01	99·14

If the small quantity of ferric oxide in *a* and *b*, β be deducted, and the magnesia and manganous oxide converted into their equivalents in ferrous oxide, the composition of these minerals may be nearly represented by the formula $FeO.TiO^2$ or $Fe''TiO^3$, which requires 53·72 TiO^2 and 46·28 FeO.—*c* is also nearly the same, but may be more closely represented by the formula $8FeO.9TiO^2$.—*d* is magnesio-ferrous titanate, $\left.\begin{matrix}\frac{1}{2}Mg\\ \frac{1}{2}Fe\end{matrix}\right\}TiO^3$, or $FeO.TiO^2 + MgO.TiO^2$, the calculated composition of which is 58·82 per cent. TiO^2, 26·47 FeO, and 14·71 MgO.

Shephard's *paracolumbite* (iv. 341) is, according to Pisani (Sill. Am. J. [2], xxxvii. 359), a ferrous titanate, difficult to separate from the matrix. It has a hardness = 4·5; specific gravity = 4·353; melts to a black magnetic bead, and gives by analysis:

TiO^2.	SiO^2.	Al^2O^3.	Fe^2O^3.	FeO.	MgO.	CaO.		
35·66	10·66	7·66	3·48	39·08	1·94	2·06	=	100·54

B. *Isomorphous Mixtures of Ferrous Titanate and Ferric Oxide.*—Titaniferous iron occurs, containing these compounds mixed in various proportions, between $9FeTiO^3.Fe^2O^3$ and $FeTiO^3.13Fe^2O^3$. The following formulæ must be regarded, not as representing definite compounds of ferrous titanate and ferric oxide, but merely as approximate expressions of the composition of the several varieties of the mineral as determined by analysis. For the discussion of the formulæ, see Rammelsberg's *Mineralchemie* (pp. 409—419).

a. From Egersund in Norway: massive; nearly black; specific gravity = 4·744—4·791 (Rammelsberg).—*b.* Krageröe, Norway: massive; specific gravity = 4·701 (Rammelsberg).—*c.* St. Paul's Bay, Canada: massive, granular, slightly magnetic; specific gravity = 4·56—4·66 (Hunt, Sill. Am. J. [2], xi. 231).—*d.* Cienaga, Province of Antioquia, New Granada (Damour, *loc. cit.*).—*e.* Ilmen Mountains, near Miask: *Ilmenite*; crystallised; powder brown-black; slightly magnetic (Rammelsberg).—*f.* Château-Richer, Canada: non-magnetic grains; specific gravity = 4·65—4·68 (Hunt).—*g.* Iserweise, in the Riesengebirge: *Iserin* (in part): granules varying in specific gravity, magnetic power, and composition; the analysis given is of a strongly magnetic grain (Rammelsberg).—*h.* Lichfield, Connecticut: *Washingtonite*; crystallised, slightly magnetic, yielding a black powder; specific gravity = 4·986 (Rammelsberg).—*i.* Eisenach, Thüringerwald: massive, yielding a black powder; not magnetic; specific gravity = 5·060 (Rammelsberg).—*j.* Uddewalla, Sweden: massive; slightly magnetic (Plantamour, J. pr. Chem. xxiv. 302).—*k.* Aschaffenburg: massive, laminar, mostly polar-magnetic; specific gravity = 4·78 (v. Kobell, *loc. cit.*).—*l.* Snarum, Norway: massive, accompanying serpentine and hydrotalcite; specific gravity = 4·943 (Rammelsberg).—*m.* St. Gothard: crystallised, yielding a black powder, non-magnetic; specific gravity = 5·187 (Rammelsberg).—*n.* Krageröe (so-called *iron-glance*); crystallised, slightly magnetic; specific gravity = 5·240 (Rammelsberg):

	TiO^2.	Fe^2O^3.	FeO.	MnO.	MgO.		
a. $9FeTiO^3.Fe^2O^3$ . .	51·30	8·87	39·83	. .	0·40	=	100·40
b. ,, ,, . .	46·92	11·48	39·82	. .	1·22	=	99·44
c. ,, ,, . .	48·60	10·16	37·30	. .	3·60	=	99·66
d. ,, ,, . .	48·14	9·45	41·66	1·69	. .	=	100·94
e. $6FeTiO^3.Fe^2O^3$ . .	45·93	14·30	36·52	2·72	0·59	=	100·06
f. $4FeTiO^3.Fe^2O^3$ . .	41·91	20·63	35·04	. .	1·51	=	99·09
g. $3FeTiO^3.Fe^2O^3$ . .	39·70	27·02	30·34	. .	2·23	=	99·29
h. $FeTiO^3.Fe^2O^3$ . .	23·72	53·71	22·39	0·25	0·50	=	100·57
i. $FeTiO^3.2Fe^2O^3$ . .	16·20	69·91	12·60	0·77	0·55	=	100·03
j. ,, ,, . .	15·56	68·31	14·00	. .	. .	=	97·87
k. $FeTiO^3.3Fe^2O^3$ . .	14·16	75·00	10·04	0·80	. .	=	100
l. $FeTiO^3.4Fe^2O^3$ . .	10·47	80·63	8·90	. .	. .	=	100
m. $FeTiO^3.5Fe^2O^3$ . .	12·67	82·49	4·84	. .	. .	=	100
n. $FeTiO^3.13Fe^2O^3$ . .	3·55	93·63	3·26	. .	. .	=	100·44

C. *taniferous Iron of abnormal composition.*—This group includes ferric titanates, ferroso-ferric titanates, and isomorphous mixtures of ferrous titanates and ferroso-ferric oxide (magnetic iron-ore).

a. Harthau, near Chemnitz: crystallised in six-sided plates (Hesse, Jahresb. 1856, p. 839).—*b.* Iserweise, in the Riesengebirge: grains with octahedral outline (probably rhombohedral, with the faces oR), occurring among the grains of iserin, having a much lower specific gravity than the latter, and rather strongly magnetic (Rammelsberg).—*c.* Unkel, on the Rhine (formerly called *scoriaceous magnetic iron-ore*): crude masses, having a conchoïdal fracture, intergrown with basalt, yielding a black powder; specific gravity = 4·905 (Rammelsberg).—*d.* On the banks of the Mersey: magnetic; specific gravity = 4·82 (Edwards, J. pr. Chem. xxi. 124):

	TiO^2.	Fe^2O^3.	FeO.	MnO.	MgO.		
a. $4Fe^2O^3.9TiO^2$ . . .	53·01	47·35	. .	. .	. .	=	100·36
b. $4(FeO.TiO^2).Fe^2O^3.3TiO^2$.	57·19	15·67	26·00	. .	1·74	=	100·60
c. $2(FeO.TiO^2).3(FeO.2Fe^2O^3)$	8·27	51·81	37·22	2·03	0·78	=	100·11
d. $3(FeO.TiO^2).5(FeO.Fe^2O^3)$	15·28	48·71	36·01	. .	. .	=	100

A titaniferous iron-ore, imbedded in the diallage and augitic gabbro of Baste in the Harz, was found by Streng (Jahresb. 1862, p. 715) to contain 45·77 per cent. TiO^2, 44·55 Fe^2O^3, and 0·56 Cr^2O^3.

Magnetic Ironsand.—In many localities, black ferruginous grains occur, strongly attracted by the magnet, and partly in the form of regular octahedrons. In a specimen from the coast of Finland, Klaproth found 14 per cent., Maly 33 per cent., titanic oxide; Cordier has found, in similar specimens, from 11 to 16 per cent. titanic oxide. In an ironsand containing octahedrons from the Etna lavas, v. Walterhausen found 12·38 per cent. TiO^2 and 92·18 Fe^2O^3, which is an excess of 4·56, indicating the presence of ferrous oxide. A specimen of very fine ironsand from the Müggel Lake, near Berlin, yielding a black powder, and having a specific gravity of 5·075, was found by Rammelsberg to contain 5·20 per cent. TiO^2, 61·36 Fe^2O^3, 30·25 FeO, 1·23 MnO, and 0·48 MgO (= 98·52), which may be nearly represented by the formula $FeO.TiO^2.6(FeO.Fe^2O^3)$; but all these substances are, perhaps, merely mixtures of ferrous titanate and magnetic iron-ore, and the occurrence of definite proportions is merely accidental.

Titaniferous Iron containing Tantalum and Niobium.—In the diamond-sand of Diamantino in Brazil, Damour found black grains, yielding a dark-green powder, and having a specific gravity of 4·82, which contained 74·32 per cent. TiO^2, 6·67 Ta^2O^5, 2·04 SnO^2, and 16·97 FeO.

According to A. E. Nordenskjöld (Pogg. Ann. cxxii. 615), a mineral resembling titaniferous iron, or ilmenite, but containing niobic as well as titanic acid, occurs near the village of Torro, in Finland.

Titanate of Magnesium.—The *monobasic salt*, $MgTiO^3 = MgO.TiO^2$, is formed by heating 1 pt. titanic oxide to whiteness for a short time in a closed vessel, with 10 pts. chloride of magnesium, and a small quantity of sal-ammoniac. On treating the fused product, first with water containing acetic acid, then with pure water, the monomagnesic titanate remains, in shining six-sided crystals, probably belonging to the trimetric system, and coloured reddish by a trace of manganese. They scratch glass, and have a density of 3·91. If the chloride of ammonium be omitted in the preparation, the proportion of magnesium in the crystals will be somewhat greater (Hautefeuille).—The *dibasic salt*, $Mg^2TiO^4 = 2MgO.TiO^2$, is obtained by fusing 2 pts. titanic oxide, 1 pt. magnesia, and 40 pts. chloride of magnesium, and proceeding as in the preparation of the corresponding ferrous salt (p. 846). It forms very brilliant regular octahedrons, harder than glass and having a specific gravity of 3·42. (Hautefeuille.)

Manganous Titanates (Hautefeuille).—The *dibasic salt*, Mn^2TiO^4, is obtained by heating titanic oxide with fluoride of manganese, but always mixed with the laminar monobasic salt; neither of these compounds has been further examined.

Titanates of Potassium.—The *monobasic salt*, $K^2TiO^3 = K^2O.TiO^2$, is obtained by fusing titanic oxide with excess of potassic carbonate. Two fused layers are then formed, the upper containing the excess of carbonate, the lower the monobasic potassium-titanate. This salt forms a yellowish, fibrous, easily fusible mass, which is resolved by water into an insoluble acid salt, and a soluble salt containing a larger proportion of base.—The *acid salt* is a soft white powder, which, after ignition, contains 17·33 to 18·01 per cent. K^2O, and 82·67 to 81·99 TiO^2. On treating it with strong hydrochloric acid, and saturating the liquid with ammonia, a precipitate is formed, which, after ignition, contains 91·3 per cent. TiO^2 to 8·7 K^2O. (H. Rose.)

A *silico-titanate of potassium* is formed by igniting titanic oxide with excess of silica and excess of potassium-carbonate, and remains behind on treating the mass with water, which dissolves out carbonate and silicate of potassium. When moist, it dissolves easily in concentrated hydrochloric acid, forming a solution, which, when boiled, deposits flocks, somewhat soluble in water, and, when mixed with ammonia, yields a precipitate of silicic and titanic acids.

Titanates of Sodium.—The *monobasic salt*, $Na^2TiO^3 = Na^2O.TiO^2$, prepared like the corresponding potassium-salt, is resolved by water into an insoluble acid salt and free soda. This acid salt forms white sandy grains, containing 15·14 to 15·30 per cent. Na^2O, 74·73 to 75·47 TiO^2, and 10·13 to 9·23 water. On treating it with strong hydrochloric acid, and neutralising with ammonia, there remains a residue containing 96·2—96·56 per cent. TiO^2 to 3·8—3·44 Na^2O. (H. Rose.)

Titanate of Zirconium is precipitated on mixing the solutions of zirconic and titanic chlorides, and adding sulphate of potassium (Berzelius). Titanate of zirconium is one of the constituents of æschynite, fergusonite, and polymignite (i. 59; iv. 55, 687).

TITANIUM, OXYCHLORIDE OF. See p. 837.

TITANIUM, OXYFLUORIDE OF. See p. 840.

TITANIUM, SULPHIDE OF. TiS^2.—This, the only known sulphide of titanium, was discovered by H. Rose, who prepared it by slowly passing the vapour of carbonic disulphide over titanic oxide, very strongly ignited in a porcelain tube. Berzelius obtained it by igniting a mixture of 1 pt. pulverised rutile, 1 pt. dry carbonate of sodium, 1 pt. sulphur, and $\frac{1}{5}$ pt. charcoal, in a crucible lined with charcoal. Larger quantities are best prepared by passing a stream of dry sulphydric acid gas into a tubulated retort, containing titanic chloride, and having its neck connected with a glass tube laid horizontally over a furnace. As soon as this tube is heated to commencing redness, the retort is warmed to such a degree, that the sulphydric acid gas may pass into the tube saturated with the vapour of titanic chloride, at a temperature somewhat below the boiling-point of the latter. Hydrochloric acid vapours are then given off, and titanic sulphide remains in the tube. (Ebelmen, Ann. Ch. Phys. [3], xx. 285.)

Titanic sulphide thus prepared forms large, brass-yellow, metallically lustrous scales, which, when rubbed on the skin, cover it with a shining coating like mosaic gold. When ignited in the air, it burns readily, yielding titanic oxide and sulphurous oxide, which is volatilised. It detonates when heated with nitre. It is decomposed by dry chlorine-gas, the products being chloride of sulphur and chloride of titanium. With nitric acid it is resolved, with rise of temperature and disengagement of nitric oxide, into titanic oxide and sulphur. It is oxidised by warm nitromuriatic acid, yielding titanic acid (the greater part of which remains undissolved) and sulphuric acid. It dissolves slowly in hydrochloric acid, with evolution of sulphydric acid (H. Rose). At a tolerably strong red heat, it decomposes vapour of water with great facility, and is converted into titanic acid, with evolution of sulphydric acid and hydrogen-gas (Regnault). It is also gradually decomposed, with evolution of sulphydric acid, by exposure to moist air. When digested with aqueous potash, it is rapidly converted into white titanate of potassium, which is precipitated, and sulphydrate of potassium, which dissolves: $TiS^2 + 2KHO = TiO^2 + 2KHS$. (Rose.)

TITANIUM-GREEN. Ferrocyanide of titanium, precipitated by ferrocyanide of potassium from a solution of titanic chloride, has been recommended as an innocuous substitute for Schweinfurt-green and other arsenical green pigments; its colour, however, is far inferior to that of Schweinfurt-green. (Elsner, Dingl. pol. J. cv. 130.—Gentele, *ibid.* clx. 238; see also Jahresb. 1847–48, p. 1058.)

TITANIUM-SAND. Pulverulent titaniferous iron (p. 847).

TITANIUM-STEEL. See IRON, ALLOYS OF (iii. 370).

TITRATION. See ANALYSIS, VOLUMETRIC (i. 254).

TIZA. Boronatrocalcite, occurring in lumps in the deposits of nitrate of soda in Peru (i. 649).

TOBACCO. This substance, so extensively used for smoking, snuffing, and chewing, is prepared from the leaves of several species of *Nicotiana*—chiefly *N. Tabacum*, Virginia tobacco; *N. macrophylla*, Maryland tobacco; *N. rustica*, and *N. quadrivalvis*. The tobacco-plant is indigenous in tropical America, but thrives, under various climatic conditions, as high as the fiftieth degree of latitude, and is extensively cultivated in most countries within those limits.

The earliest chemical investigation of tobacco-leaves is that of Posselt and Reimann (Geiger's Mag. xxiv. 138; xxv. [2], 57), who found, in 1,000 pts.:

Nicotine	0·6	Malic acid, malates, and nitrates	9·7
Nicotianine	0·1	Other potassium-salts	1·2
Bitter extractive	28·7	Phosphate of calcium	1·7
Resin	2·7	Woody fibre, water, &c.	924·8
Albumin and Glutin	13·1		
Gum	17·4		

According to later investigations, the proportion of the poisonous alkaloïd, nicotine, is much larger. Schlösing (Ann. Ch. Phys. [3], xix. 230) found, in different sorts of tobacco, from 2 to 8 per cent. nicotine, the better and milder varieties, such as that from Havannah, containing the smallest quantity. (See NICOTINE, iv. 45.)

Another volatile constituent of tobacco is nicotianine, or tobacco-camphor (iv. 44). Vauquelin (Ann. Chim. lxxi. 139) found in tobacco an organic acid, which he regarded as malic acid, a result confirmed by Posselt and Reimann. Barral (Compt. rend. xxi. 1374) regarded it as a peculiar acid, designating it as nicotic acid. According to Goupel (Ann. Ch. Phys. [3], xvii. 503), the acid of tobacco-leaves is malic acid with a little citric acid: from 100 grms. of the dried leaves he obtained from 3 to 4 grms. of acid ammonium-malate.

Tobacco contains a considerable amount of inorganic constituents, the dried leaves yielding from 18 to 23 per cent. of ash. According to Casaseca (Ann. Ch. Phys. [3], xlv. 479), good Havannah tobacco contains from 16 to 16·8 per cent. ash; inferior sorts from 17·8 to 19·4 per cent.; the latter contained a trace of iodine, which was not found in the better kinds. Vogel (Repert. Pharm. [1858], vi. 100) found, in Turkish tobacco from various localities, 17 to 23 per cent.; in Russian, 21·9 to 24·9; in Grecian, 19 per cent. ash. Will and Fresenius (Ann. Ch. Pharm. l. 387) have analysed the ash of several varieties of Hungarian tobacco (No. i. to viii. of the following table), and Merz (*ibid.* lxxix. 109) has analysed that of tobacco grown in the neighbourhood of Nürnberg (No. ix.):—

Ash of Tobacco.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Ash per cent. of dry substance:									
Leaves	18·9	19·8	23·0	21·1	23·3	23·3	22·8	27·3	
Stalks	22·9	32·5	19·8						
Potash	29·1	18·8	8·2	19·5	9·7	9·3	10·3	11·2	26·9
Soda	2·2	. .	. .	0·3	. .	. .	. .	. .	2·7
Lime	27·7	27·8	42·8	44·5	49·3	49·4	39·5	47·0	39·5
Magnesia	7·2	15·7	13·9	11·1	14·6	15·6	15·0	12·8	9·6
Chloride of sodium	0·9	11·4	2·2	3·5	4·6	3·2	6·4	2·6	9·6
Chloride of potassium	. .	3·9	8·5	. .	4·4	3·3	3·0	3·0	
Ferric phosphate	8·8	6·8	6·1	4·3	5·2	6·7	7·5	6·3	4·2
Phosphate of calcium	. .	. .	. .	6·0					
Sulphate of calcium	6·4	10·1	8·0	5·6	6·7	6·1	9·4	5·1	
Silica	17·6	6·0	9·3	5·1	5·5	6·3	8·3	12·0	4·5
Sulphuric anhydride	. .	. .	. .	. .	. .	. .	. .	. .	2·8
	99·9	100·5	99·0	99·9	100·0	99·9	99·4	100·0	99·8

Schlösing (J. pr. Chem. lxxxi. 148) has determined the quantities of potash, lime, magnesia, sulphuric acid, and chlorine in tobacco grown on various soils. In the air-dried leaves of twelve different sorts, he found 90 pts. of dry substance and 10 pts. water:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Potash	1·0	1·0	2·6	1·7	2·1	1·6	2·2	2·5	1·1	0·8	1·4	2·0
Lime	7·7	7·5	6·6	7·2	6·2	7·3	6·2	6·6	8·5	8·3	7·7	7·4
Magnesia	1·0	0·8	0·8	0·7	0·6	. .	0·6	. .	1·0	1·1	0·9	0·3
Sulphuric anhydride	1·0	0·9	1·0	0·9	0·8	1·0	0·8	1·0	0·8	0·8	1·0	1·0
Chlorine	0·7	0·5	0·4	1·6	0·4	0·4	0·4	0·5	1·8	1·7	. .	0·5

The combustibility of tobacco is influenced to a considerable extent by the proportion of the potash and lime contained in it, and the manner in which these bases are combined with acids. The ash of the more combustible tobaccos is comparatively rich in carbonate of potassium, showing that in these tobaccos the potash is in combination with organic acids; whereas the ash of the less combustible tobaccos contains sulphate and chloride of potassium, together with carbonate of calcium, instead of carbonate of potassium, showing that in these tobaccos the organic acids are combined with lime. A slowly-burning tobacco may be rendered more combustible by adding to it an organic potassium-salt, in such quantity that the amount of potash in the ash may be more than equivalent to the sulphuric and hydrochloric acids present; and, on the other hand, the combustibility of tobacco may be diminished by mixing it with such a quantity of sulphate or chloride of magnesium, calcium, or ammonium, that the amount of hydrochloric or sulphuric acid in the ash may be more than equivalent to the potash, so that the ash will not contain any potassic carbonate. (Schlösing.)

Tobacco always contains nitrates. According to Schlösing, these salts are most abundant in the midrib of the leaf, which, in different varieties, contains from 0·15 to 6·1 per cent. nitric acid, the leaf, deprived of its midrib, containing from 0·02 to 2·0 per cent. The ready inflammability of tobacco, and its capability of burning with a smouldering flame, are due, in great part, to this large amount of nitrates.

In the smoking of tobacco an imperfect combustion takes place, one part of the tobacco burning in contact with the air, and producing by its combustion a quantity of heat sufficient to decompose the remainder by destructive distillation, producing water and tar (oil of tobacco), which, when the tobacco is smoked in a pipe, condense as liquid products. Tobacco-smoke consists partly of permanent gases—namely, carbonic oxide, carbonic dioxide, and perhaps also one or more hydrocarbons—partly of condensable vapours, including, according to Zeise (Ann. Ch. Pharm. xlvii. 212), ammonia, butyric acid, probably also acetic acid, paraffin, empyreumatic oil, and resin, but no creosote. Melsens found nicotine, the presence of which is, indeed, sufficiently indicated by the narcotic action of the tobacco-smoke. Vogel (Repert. Pharm. vi. 1 155; vii. 97, 514; viii. 145) found sulphydric and hydrocyanic acids, and determined their quantity, as well as that of the ammonia: from 100 grms. tobacco he obtained 0·7 to 2·8 grms. ammonia. The proportions of the several constituents of tobacco-smoke vary, of course, according to the freedom of access of air during the combustion: hence the difference in the action of tobacco, according as it is smoked in pipes or in cigars.

Respecting the manufacture of tobacco and snuff, see *Ure's Dictionary of Arts*, &c., iii. 907; *Handw. d. Chem.* viii. 462.

TOBACCO-CAMPHOR. Syn. with Nicotianine (iv. 44).

TOBACCO-OIL. The empyreumatic oil produced in the destructive distillation of tobacco.

TOBACCO-SEED OIL. Tobacco-seeds are said to yield, by pressure, about 36 per cent. of a greenish-yellow, mild, inodorous oil, of specific gravity 0·923 at 15°, solidifying at −25°, and quickly drying when exposed to the air.

TODDALEA. See Lopez-root (iii. 733).

TOLALLYL-SULPHIDE. $(C^7H^5)^2S$.—A product obtained, together with others, by the dry distillation of sulphide or disulphide of benzyl. After repeated crystallisation from alcohol, it forms a white crystalline powder, very sparingly soluble in alcohol, more easily in ether or in benzene, and melting at 143°—145°. (Märcker, Ann. Ch. Pharm. cxxxvi. 75.)

TOLENE. $C^{10}H^{16}$.—The oily constituent of tolu-balsam (i. 498). The balsam distilled with water yields 0·2 per cent. of the oil (Deville), 1·1 per cent. (Scharling), which may be rectified over hydrate of potassium. Scharling further treats it with potassium, and then rectifies it again.

Tolene is a colourless very mobile liquid, having a pungent odour, and a specific gravity of 0·858 at 10° (E. Kopp). It boils at 170° (Deville; Scharling), at 154°—160° (E. Kopp). Vapour-density = 5·1 (Deville). When exposed to the air, it quickly takes up oxygen, and becomes resinised; it likewise oxidises when boiled with water and mercuric oxide, forming a small quantity of carbonic anhydride; but the oxidation is not easily completed, and does not yield any well-characterised products (Schorling). Tolene mixed with bromine forms a black-brown tarry liquid.

TOLID. A name sometimes applied to benzyl, C^7H^7.

TOLIN. Syn. with Toluene.

TOLU-BALSAM. See Balsams (i. 498).

TOLUAMIC ACID. $C^8H^9NO^2$.—Syn. with Oxytoluamic Acid (iv. 321).

TOLUENE, or **TOLUOL.** C^7H^8.—Syn. with Benzylic Hydride, under which name the compound has been already described (i. 574).

Besides the modes of formation there mentioned, it is produced:—*α*. By distilling vulpic or oxytolic acid with potassium-hydrate (Möller and Strecker, Ann. Ch. Pharm. cxiii. 69).—*β*. In the dry distillation of several organic substances, namely of dragon's-blood (Glénard and Boudault, *ibid.* liii. 325), wood (Cahours; Volckel), and coal (Mansfield), being, in fact, a constant constituent of coal-tar oil.—*γ*. By the action of methyl-iodide and sodium on monobromobenzene (Fittig and Tollens):

$$C^6H^5Br + CH^3I + Na^2 = NaBr + NaI + C^7H^8.$$

This and the following mode of formation show that toluene may be regarded as methylic benzene, $C^6H^5(CH^3)$, or phenyl-methyl, $C^6H^5.CH^3$.

δ. By the mutual action of benzene and methylic hydride (marsh-gas) in the nascent state, as when an intimate mixture of 2 pts. acetate and 1 pt. benzoate of sodium is subjected to dry distillation (Berthelot, Bull. Soc. Chim. [1867], i. 116):

$$C^6H^6 + CH^4 = C^7H^8 + H^2.$$

Other homologues of benzene—namely, xylene, C^8H^{10}, and cumene, C^9H^{12}—are produced at the same time by similar reactions. The formation of these homologues of benzene in the destructive distillation of coal is probably due, in like manner, to the reaction of benzene and marsh-gas at the moment of their elimination from certain constituents of the coal.—ε. Toluene is found, together with many other hydrocarbons, in Rangoon tar (iv. 3).

Toluene is most advantageously prepared from coal-naphtha; in fact, the coal-naphtha now occurring in commerce consists mainly of toluene and its higher homologues. It may be obtained tolerably pure by collecting the portion of the naphtha which distils between 100° and 120°, agitating it with half its weight of strong sulphuric acid, and rectifying it repeatedly, collecting apart the portion which distils between 108° and 110°.

Toluene has a specific gravity of 0·8654 at 15° (Mendelejef, Jahresb. 1860, p. 7); 0·8824 at 0°, 0·8720 at 15° (Warren, *ibid.* 1865, p. 525). It boils at 110·3° (corrected). (Warren.)

Toluene-vapour passed through a porcelain tube heated to bright redness, is decomposed, yielding uncondensable gases and a tarry liquid, which may be resolved, by two series of rectifications, into benzene, C^6H^6; unaltered toluene, C^7H^8; naphthalene, $C^{10}H^8$; benzyl, $C^{14}H^{14}$, and a hydrocarbon apparently isomeric therewith; anthracene, $C^{14}H^{10}$, chrysene, $C^{18}H^{12}$; and hydrocarbons of higher atomic weight. The formation of these hydrocarbons may be represented by the equations:

$$\underset{\text{Toluene.}}{2C^7H^8} = \underset{\text{Benzyl.}}{C^{14}H^{14}} + H^2.$$

$$\underset{\text{Toluene.}}{4C^7H^8} = \underset{\text{Benzene.}}{3C^6H^6} + \underset{\text{Naphthalene.}}{C^{10}H^8} + 3H^2.$$

$$\underset{\text{Toluene.}}{2C^7H^8} = \underset{\text{Anthracene.}}{C^{14}H^{10}} + 3H^2.$$

$$\underset{\text{Toluene.}}{18C^7H^8} = \underset{\text{Chrysene.}}{7C^{18}H^{12}} + 30H^2.$$

Or the chrysene may be formed from benzene, according to the equation $3C^6H^6 = C^{18}H^{12} + 3H^2$. (Berthelot, Bull. Soc. Chim. [1837], i. 218.)

Toluene oxidised with dilute nitric acid yields oxytolic acid, $C^7H^6O^3$ (Fittig, iv. 321); but fuming nitric acid converts it into nitrodracylic acid, $C^7H^4(NO^2)O^2$, isomeric with nitrobenzoic acid (iv. 60).

Derivatives of Toluene.

The rational formula of toluene, $C^6H^5.CH^3$, indicates the existence of two series of substitution-products, according as the hydrogen of the phenyl-molecule, or of the methyl-molecule, is replaced by other radicles, *e.g.*:

$C^6H^4Cl.CH^3$ Monochlorotoluene.	$C^6H^5.CH^2Cl$ Benzylic chloride.
$C^6H^4(HO).CH^3$ Cresol.	$C^6H^5.CH^2(HO)$ Benzylic alcohol.
$C^6H^4(NH^2).CH^3$ Toluidine.	$C^6H^5.CH^2(NH^2)$ Benzylamine.

These isomeric derivatives differ considerably from one another in their properties. Those in the left-hand column, formed by replacement of hydrogen in the phenyl-molecule, are comparatively stable and indifferent compounds, like those derived in like manner from benzene, C^6H^6; whereas those in the right-hand column, formed by replacement of hydrogen in the methyl-molecule, are more active bodies, capable of easily exchanging their chlorine, hydroxyl, &c. for other radicles by double decomposition. Thus benzylic alcohol, treated with hydrochloric acid, yields benzylic chloride; this compound, heated with alcohol ammonia, yields benzylamine; the chloride is also easily converted into the acetate, cyanide, &c. by treatment with the corresponding potassium-salts. In short, these last-mentioned toluene-derivatives exhibit reactions exactly like those of the corresponding compounds of the fatty series, and may, in like manner, be supposed to contain an alcohol-radicle, C^7H^7, called benzyl or tolyl, and referred to the water-type, ammonia-type, &c.: *e.g.*, benzylic chloride $= C^7H^7.Cl$; benzylic alcohol $= C^7H^7.H.O$; benzylamine $= C^7H^7.H^2.N$, &c.

Amidotoluene, $C^7H^9N = C^7H^7(NH^2) = C^6H^4(NH^2).CH^3$. Syn. with TOLUIDINE (p. 865).

Azotoluenes. See AZOTOLUIDINES (p. 867).

Bromotoluenes. (Glinzer and Fittig, Ann. Ch. Pharm. cxxxiii. 47; cxxxvi.

301.—Kekulé, Ann. Ch. Pharm. cxxxvii. 183, 192.—Lauth and Grimaux, Bull. Soc. Chim. [1866], i. 647; [1867], i. 108).—Bromine acts directly upon toluene, forming monobromotoluene, or benzylic bromide, according as the reaction takes place at low or at high temperatures. Higher substitution-products appear to be formed at the same time, but they have not been isolated.

MONOBROMOTOLUENE, $C^7H^7Br = C^6H^4Br.CH^3$, is prepared by gradually adding bromine to toluene kept cool and in excess, leaving the liquid to itself for a few days, and purifying the product by agitation with potash-ley, and rectification over solid potash. It is a colourless liquid, having a faint, not unpleasant odour when cold, but (according to Lauth and Grimaux) extremely irritating to the eyes when heated; according to Fittig and Kekulé, on the other hand, pure bromotoluene does not exhibit this irritating property. It has a specific gravity of 1·4092 at 15°, and boils at 179° (Glinzer and Fittig); at 181° (Lauth and Grimaux); at 182·5°—183° (Kekulé). It is a very stable compound, and is not decomposed by heating with ethylate of sodium, acetate of potassium, acetate of silver, cyanide of potassium, or alcoholic ammonia.

Benzylic bromide, $C^7H^7.Br = C^6H^5.CH^2Br$, is easily obtained by the action of gaseous hydrobromic acid, or the saturated aqueous acid, on benzylic alcohol; also by the action of bromine on boiling toluene. It is a colourless liquid, fuming slightly in the air, and boiling at 198°—199° (Kekulé); at 202°, according to Lauth and Grimaux; but their product was probably impure. It has at first a pleasant aromatic odour, but exposure to its vapour produces a copious flow of tears. It gives up its chlorine, by double decomposition, with great facility, being rapidly attacked by acetate of potassium, acetate of silver, cyanide of potassium, alcoholic solution of hydrate or sulphydrate of potassium, and alcoholic ammonia, yielding benzyl-compounds in all cases.

DIBROMOTOLUENE, $C^7H^6Br^2$.—Toluene is capable of yielding three dibrominated derivatives, corresponding to the dichlorinated toluenes (p. 854); but the only one hitherto obtained in the pure state is that which corresponds to chlorobenzol, viz. dibromobenzol, or bromide of benzylidene, $C^7H^6.Br^2 = C^6H^5.CBr^2H$, which is produced by the action of phosphoric pentabromide on benzoic hydride (bitter-almond oil). It is decomposed by distillation under the ordinary atmospheric pressure, but distils easily in a vacuum. When treated with sodium, or sodium-amalgam, it yields toluene and benzyl, $C^{14}H^{14}$ (Michaelson and Lippmann, Ann. Ch. Pharm. Supp. iv. 113). See p. 870.

Lauth and Grimaux have likewise obtained other brominated derivatives of toluene, but not in sufficient quantity for accurate investigation.—*α*. If the first drops of bromine be added very slowly to the toluene, no disengagement of hydrobromic acid takes place; but the mixture, which remains colourless, deposits a small quantity of a compound in hexagonal tables, perhaps resulting from the direct fixation of bromine on toluene.—*β*. When the crude bromotoluene is distilled till the boiling-point rises to 185°, a black viscid residue is left, extremely irritating to the eyes, and becoming filled, after a few days, with needle-shaped crystals, difficult to purify from a thick viscid substance with which they are impregnated.—*γ*. When toluene was treated with 2 at. bromine (for the preparation of dibromotoluene), a thick liquid was formed, which remained coloured even after the excess of bromine had been removed. This liquid, when distilled, began to boil at 187°, continued to give off hydrobromic acid till the temperature rose to 210°, and left a black residue which did not solidify.

Chlorotoluenes.—The action of chlorine upon toluene gives rise to a number of substitution-products, differing in constitution according as the reaction takes place at high or at low temperatures. Compounds isomeric with some of these are also obtained from benzylic alcohol.

Of the two monochlorinated compounds whose existence is indicated by theory, viz. monochlorotoluene and benzylic chloride, the former is produced at low, the latter at high temperatures, as is the case with the corresponding bromine-compounds.

MONOCHLOROTOLUENE, $C^6H^4Cl.CH^3$.—Deville obtained this compound by saturating toluene (prepared from tolu-balsam) with chlorine (i. 574); and Beilstein and Geitner have lately shown (Ann. Ch. Pharm. cxxix. 331; Bull. Soc. Chim. [1867], i. 251), that it is always produced when cooled toluene is treated with chlorine. As, however, the action is attended with rise of temperature, benzylic chloride is apt to be produced at the same time; but pure chlorotoluene may be obtained by treating the crude product with any of the reagents by which benzylic chloride is decomposed. Pure chlorotoluene, free from benzylic chloride, is also produced at once by treating toluene with chlorine in presence of iodine. The same compound is probably formed by the action of chlorine on cresol.

titanate, with silica at a high temperature. Deville finds also (Compt. rend. lii. 1864), that the amorphous oxide is converted into quadratic crystals (like rutile or anatase) by ignition in hydrochloric acid gas; the crystals are coloured blue, in consequence of the formation of a small quantity of a lower oxide. Hautefeuille (Compt. rend. lvii. 148; lx. 188; Jahresb. 1863, p. 212; 1864, p. 213) has also obtained crystallised titanic oxide by two methods: *α.* By decomposing titanic chloride or fluoride with aqueous vapour.—*β.* By crystallising amorphous titanic oxide in an atmosphere hydrochloric or hydrofluoric acid. The second method is, however, only a modification of the first, inasmuch as titanic chloride or fluoride is first formed, and subsequently decomposed. Under the influence of hydrochloric acid, the formation of crystallised titanic oxide takes place only at very high temperatures, and the crystals produced have always the form of rutile: under the influence of hydrofluoric acid, on the contrary, anatase is formed at the lowest red heat, brookite at a somewhat higher temperature, and rutile at very high temperatures.

Anhydrous titanic oxide melts only at the heat of the oxyhydrogen-blowpipe. It is completely insoluble in water, and in all acids excepting strong sulphuric acid. When heated in the pulverised state with this acid till the excess is driven off, the residue dissolves in water after cooling. By fusing the anhydrous oxide with six times its weight of acid potassic sulphate, a clear yellow mass is obtained, which dissolves perfectly in warm water, forming a clear solution.

Potassium and *sodium* reduce titanic oxide at a red heat, forming oxide of potassium or sodium, and a black mass, which does not acquire metallic lustre, and appears to be a mixture of metallic titanium with titanic or titanous oxide.—*Charcoal*, at white heat, reduces titanic oxide to the metallic state.—*Carbonic disulphide*, at a strong red heat, converts titanic oxide into sulphide of titanium, with simultaneous formation of carbonic oxide and carbonic dioxide (H. Rose).—When dry *chlorine-gas* is passed over an ignited mixture of titanic oxide and charcoal, titanic chloride is produced (p. 837). The oxide, fused with *alkaline carbonates*, yields titanates of alkali-metal.—*Ammonia-gas*, at a bright red heat, reduces titanic oxide to violet nitride of titanium, TiN^2 (Elsner.)

TITANIC HYDRATES OR ACIDS.—There appear to be two modifications of titanic acid, analogous in some respects to stannic and metastannic acid.—*α.* One of these, called titanic acid, is precipitated by ammonia from the solution of titanic chloride. It is a white powder, of specific gravity 3·8 to 3·93 according as it has been exposed to a higher or lower temperature. When heated, it assumes a transient yellow colour, becoming white again on cooling. Its conversion into titanic oxide, at a higher temperature, is attended with vivid incandescence.

Titanic hydrate dissolves easily in sulphuric, nitric, and hydrochloric acids, even when these acids are rather dilute; but these dilute solutions, when boiled, deposit metatitanic hydrate as a soft white powder, which, like anhydrous titanic oxide, is quite insoluble in all acids, excepting strong sulphuric acid. It also resembles the anhydrous oxide in not exhibiting incandescence when heated. Titanic hydrate, precipitated by ammonia, is also converted into insoluble metatitanic hydrate by washing with hot water, or drying at a high temperature.—According to R. Weber (Pogg. Ann. cxx. 287; Jahresb. 1863, p. 210), a recently prepared aqueous solution of titanic chloride is not clouded by sulphuric, nitric, or hydrochloric acid, but phosphoric, arsenic, and hydriodic acids give precipitates with it immediately, and acid potassic chromate after some time. If, however, the same solution be heated to the boiling-point for only a few seconds, it immediately yields, with hydrochloric, nitric, sulphuric, hydrofluoric, and even organic acids, a white precipitate of metatitanic hydrate, and with dichromate of potassium an immediate orange-yellow precipitate. The precipitated metatitanic hydrate dissolves completely in a large quantity of water, after the supernatant acid has been poured off, and is reprecipitated from the solution by acids. Metatitanic acid is also produced by oxidising metallic titanium with nitric acid of specific gravity 1·25. (Weber.)

Titanic hydrate dried over oil of vitriol, has, according to H. Rose, the composition, H^2TiO^3, or $H^2O.TiO^2$, but always contains a little ammonia which cannot be removed by washing. According to Merz (*loc. cit.*), titanic hydrate, after drying in the air for twenty-four hours, contains $H^2TiO^3.2H^2O$; after drying for several weeks, $H^2TiO^3.H^2O$. When dried over oil of vitriol, it quickly loses 1 at. water; and after being left for some time over oil of vitriol, or dried at 60°, it contains $3H^2TiO^3.TiO^2$, and finally, after drying at 100°, $H^2TiO^3.TiO^2$.

Metatitanic acid, deposited from its solution in sulphuric acid on boiling, contains, after prolonged drying in the air, or for twenty-four hours over oil of vitriol, H^2TiO^3; at 60°, it contains $H^2TiO^3.TiO^2$; at 100°, $H^2TiO^3.2TiO^2$; at 120°, $H^2TiO^3.3TiO^2$; at 160°, $H^2TiO^3.4TiO^2$. In short, metatitanic acid gives up its water more easily than titanic acid. (Merz.)

Chlorobenzylic chloride, $C^6H^4Cl.CH^2Cl$ (often called *Dichlorotoluene*).—This compound is produced, as above stated, by the action of chlorine on benzylic chloride, or on monochlorotoluene, and therefore also by the action of chlorine on toluene. Beilstein (Ann. Ch. Pharm. cxvi. 336) saturates toluene in diffused daylight with chlorine, either at ordinary or at higher temperatures; distils, collecting the product which passes over between 186° and 220°; and rectifies it several times. It is difficult to obtain a product of constant boiling-point; that of the pure compound appears to be somewhat below 200°. (Compare Lauth and Grimaux, Bull. Soc. Chim. [1867], i. 108).

Chlorobenzylic chloride is a colourless, strongly refracting liquid, the vapours of which excite tears. It easily gives up one-half of its chlorine, but the other half is more fixed, as in true substitution-products.—With *alcoholic potash*, it yields a chlorinated oil, $C^9H^{11}ClO$, boiling at 215°—220°, which is the ethylic ether of monochlorinated benzyl-alcohol, $\left.\begin{matrix}C^7H^6Cl\\H\end{matrix}\right\}O$ (Naquet, Ann. Ch. Pharm. Suppl. ii. 249); and with *alcoholic sulphide of potassium*, a beautifully crystallised compound, which is the sulphydrate or mercaptan corresponding to the same alcohol, $\left.\begin{matrix}C^7H^6Cl\\H\end{matrix}\right\}S$ (Beilstein). Chlorobenzylic chloride is not converted into benzoic hydride by heating with water to 130°—140°; neither does it yield benzoic acid on exposure to moist air. (Naquet.)

Chlorobenzol, $C^7H^6Cl^2 = C^6H^5.CCl^2H$. (Cahours, Ann. Ch. Pharm. lxx. 39; *ibid.* Suppl. ii. 253, 306.—Wicke, Ann. Ch. Pharm. cii. 356.—Engelhardt, Jahresb. 1857, p. 470.—Naquet, Ann. Ch. Pharm. Suppl. ii. 249, 258.)—This compound, already described as chloride of benzylene, $(C^7H^6)''Cl^2$ (i. 577), is produced by the action of phosphoric pentachloride on benzoic hydride. According to Lauth and Grimaux (Bull. Soc. Chim. [1866], ii. 347), it is also formed, together with benzylic and chlorobenzylic chlorides, when toluene is distilled in a current of chlorine, and remains in the retort, together with chlorobenzylic chloride, after the benzylic chloride has been distilled off.

Chlorobenzol is a colourless, strongly refracting oil, having a faint odour in the cold, strongly irritating when heated, and boiling at 206°. Specific gravity = 1·295 at 16°. It gives up the whole of its chlorine with great facility, in exchange for *oxygen*, producing benzoic hydride, the reaction being, in fact, the opposite of that by which it is produced:

$$C^6H^5.CCl^2H + H^2O = C^6H^5.COH + 2HCl.$$

Thus, when heated with water or aqueous potash to 120°—130°, it is converted into benzoic hydride; and in contact with moist air, it yields benzoic acid, evidently resulting from oxidation of the previously formed hydride (Cahours). Heated with *alcoholic sulphydrate of potassium*, it yields the sulphur-analogue of benzoic hydride, C^7H^6S, commonly called *sulphobenzol* (Cahours).—*Sodium* decomposes it, forming chloride of sodium, and benzylene, C^7H^6. When its vapour is directed upon ignited *soda-lime*, benzene is formed, together with carbonic oxide and hydrochloric acid (Limpricht, Bull. Soc. Chim. 1866, ii. 467):

$$C^7H^6Cl^2 + H^2O = C^6H^6 + CO + 2HCl.$$

Trichlorotoluene, and its isomers.—Of the numerous isomeric compounds which might be included under the empirical formula $C^7H^5Cl^3$, only two are known with certainty, viz.:

$C^6H^3Cl^2.CH^2Cl$	and	$C^6H^5.CCl^3$.
Dichlorobenzylic chloride.		Benzotrichloride.

The true trichlorotoluene, $C^6H^2Cl^3.CH^3$, may perhaps be formed by the action of chlorine on toluene, but it has not been isolated.

Dichlorobenzylic chloride, $C^6H^3Cl^2.CH^2Cl$.—This compound is formed by the prolonged action of chlorine upon toluene, and separated by repeated fractional distillation (Naquet, Ann. Ch. Pharm. Suppl. ii. 248). It is commonly regarded as trichlorotoluene, but, according to Kekulé (*Lehrbuch*, ii. 561), it should rather be regarded as a substitution-derivative of benzylic chloride, inasmuch as its formation is preceded by that of monochlorobenzylic chloride. It is a colourless liquid, having a pungent odour, and a specific gravity of 1·44. Under the ordinary atmospheric pressure, it boils, with partial decomposition, at 240°; but under a reduced pressure of 10 mm. of mercury, it distils without decomposition at 135°—143°. It may be heated with water to 200° for several days, without forming benzoic acid; according to Naquet, however, it yields that acid when strongly heated with alcoholic potash.

Benzotrichloride, or *Chlorinated Chlorobenzol*, $C^6H^5Cl^3$. (Schischkoff and Rosing, Jahresb. 1858, p. 279.—Cahours, Ann. Ch. Pharm. Suppl. ii. 306.—

Limpricht, *ibid.* cxxxiv. 55, cxxxv. 80; Bull. Soc. Chim. 1866, ii. 468.)—This substance, analogous in composition and properties to chloroform, was discovered, in 1848, by Schischkoff and Rosing, who obtained it by the action of phosphoric pentachloride on benzoic chloride, to which it is related in the same manner as chlorobenzol to benzoic hydride:

$$\underset{\text{Benzoic chloride.}}{C^6H^5.COCl} + PCl^5 = \underset{\text{Benzotrichloride.}}{C^6H^5.CCl^3} + POCl^3.$$

To prepare it, benzoic chloride is heated with pentachloride of phosphorus to 180° for 48 hours. It is also formed by the action of chlorine on chlorobenzol. (Cahours.)

Benzotrichloride is a liquid smelling like benzoic chloride, and boiling at 215°—218°. It is insoluble in water, by which, however, it is converted (slowly in the cold, quickly at 140°) into benzoic acid.—*Sodium* does not act upon it, even at the boiling heat.—Dry *silver-oxide* converts it into benzoic anhydride; with silver-oxide moistened with alcohol, it forms benzoic acid and benzoic ether. When heated with *alcohol* to 130°, it likewise yields benzoic acid, according to the following equation:

$$C^7H^5Cl^3 + 3(C^2H^5.H.O) = C^7H^6O^2 + 3C^2H^5Cl + H^2O.$$

Sulphydrate of potassium in alcoholic solution acts upon it, with evolution of heat, forming a crystallisable sulpho-compound, not yet investigated.

Benzotrichloride heated to 140°, with aqueous *ammonia*, yields a large quantity of benzonitrile, behaving in this respect just like chloroform:

$$C^7H^5Cl^3 + NH^3 = C^7H^5N + 3HCl.$$

It also reacts like chloroform with *ethylate of sodium*, forming a compound (boiling at 220°—225°), analogous to the so-called tribasic formic ether:

$$C^7H^5Cl^3 + 3C^2H^5NaO = 3NaCl + \left.\begin{matrix}(C^7H^5)'''\\(C^2H^5)^3\end{matrix}\right\}O^3.$$

With *acetate of silver*, it forms, in the first instance, a compound, $C^{13}H^{14}O^6$, which may be regarded either as an acetyl-compound $\left.\begin{matrix}(C^7H^5)'''\\(C^2H^3O)^3\end{matrix}\right\}O^3$, analogous to the ethylic ether just mentioned, or as a compound of acetic and acetobenzoic anhydride, $\left.\begin{matrix}C^2H^3O\\C^7H^5O\end{matrix}\right\}O . \left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}O$. This body decomposes easily, apparently with separation of acetic anhydride, and leaves a crystalline compound, which has the composition of acetobenzoic anhydride, $\left.\begin{matrix}C^2H^3O\\C^7H^5O\end{matrix}\right\}O$, and separates, after a while, into acetic and benzoic anhydrides. (Limpricht.)

With *aniline*, benzotrichloride forms a base, $C^{19}H^{16}N^2 = \left.\begin{matrix}(C^7H^5)'''\\(C^6H^5)^2\\H\end{matrix}\right\}N^2$, which yields crystallisable salts. (Limpricht.)

TETRACHLOROTOLUENE, $C^7H^4Cl^4$, and its isomers.—A body having this composition, and probably consisting of trichlorobenzylic chloride, $C^6H^2Cl^3.CH^2Cl$, is found among the products of the action of chlorine on toluene. It forms needles, melting at 96°, and boils without decomposition at 276°. It is not decomposed by heating with water to 230°. (Limpricht.)

Chlorobenzoic trichloride, $C^6H^2ClH^2.CCl^3$, the analogue of the true chlorobenzoic acid, is produced (together with benzotrichloride) by the action of phosphoric pentachloride on chloride of benzoyl. It is a liquid, boiling at 250°, not solidifying at 0°, and converted into chlorobenzoic acid by heating with water (Limpricht). Identical with this is the tetrachloride, which was found by Kämmerer and Carins (Ann. Ch. Pharm. cxxx. 158) among the products of the action of phosphoric pentachloride on chloride of benzoyl; also that which Cahours obtained (*ibid.* Suppl. ii. 251) by the action of chlorine on chlorobenzol. Kolbe and Lautemann (*ibid.* cxv. 195), by distilling salicylic acid with pentachloride of phosphorus, obtained a tetrachloride isomeric with the preceding, and perhaps consisting of $C^6H^3ClH.CCl^3$. It melted at 30°, and, when heated with water to 150°, was converted into chlorosalylic acid, isomeric with chlorobenzoic acid. (See p. 185.)

PENTACHLOROTOLUENE, $C^7H^3Cl^5$.—A body having this composition is said by Limpricht to be obtained, together with previously described products, by the action of phosphoric pentachloride on chloride of benzoyl.

HEXCHLOROTOLUENE, $C^7H^2Cl^6$.—A body of this composition was obtained by Deville (Ann. Ch. Pharm. xliv. 304) as the final product of the action of chlorine on toluene (from tolu-balsam). A body of the same composition, and perhaps identical therewith, was obtained by Cahours, by treating chlorobenzol with chlorine. It forms silky needles, which sublime without decomposition, and may be recrystallised from ether.

Respecting the dihydrochlorate and trihydrochlorate of pentachlorotoluene, obtained by Deville, see i. 574.

Ethyltoluene, $C^9H^{12} = C^7H^7(C^2H^5) = C^6H^4(C^2H^5).CH^3$. (Glinzer and Fittig, Ann. Ch. Pharm. cxxxvi. 303; Jahresb. 1865, p. 537.)—This compound, homologous with ethylbenzene or phenyl-ethyl (iv. 484), is produced by the action of sodium on a mixture of bromotoluene and ethylic bromide. It has a peculiar odour, like that of methyltoluene (*infra*), boils at 159°—160°, and has a specific gravity of 0·8652 at 21°. From the isomeric body cumene (obtained from cuminic acid or from coal-tar), it is distinguished by its boiling-point (cumene boiling at 144°—148°), and from mesitylene, with which it is likewise isomeric, by its behaviour with reagents.—Cold fuming *nitric acid* converts it into an oily, non-distillable nitro-compound, probably $C^9H^{10}(NO^2)^2$.—With warm *nitric acid*, it forms trinitro-ethyltoluene, $C^9H^9(NO^2)^3$, which separates in large apparently rhombohedral crystals, melting at 92°.—*Chromic acid* oxidises it to terephthalic acid.

Hydroxyltoluene. Cresol. Cresylic Alcohol. $C^7H^8O = C^6H^4(OH).CH^3$.—This compound, isomeric with benzylic alcohol, $C^6H^5.CH^2(OH)$, and related to toluene in the same manner as phenol to benzene, has already been described, under the last-mentioned name (ii. 106), as a colourless, strongly refracting liquid, obtained from coal-tar and the tar of fir-wood. It is, however, produced in a state of greater purity from toluidine—namely, by treating nitrate of toluidine with nitrous acid, converting the resulting nitrate of diazotoluene into sulphate, and decomposing this compound by boiling with water (p. 867). As thus prepared, it is solid and crystalline.

The nitrocresols are described under CRESYLIC ALCOHOL (ii. 106). Amidodinitrocresol, $C^7H^5(NO^2)^2(NH^2)$, is produced by saturating an alcoholic solution of trinitrocresol, first with ammonia, then with sulphydric acid gas. The deep red liquid is evaporated to dryness, the residue exhausted with ammoniacal water, and the filtered solution acidulated with very dilute sulphuric acid, whereby the amidodinitrocresol is thrown down as a very dark-coloured precipitate, which may be purified by repeated crystallisation from hot water or hot alcohol. It then forms yellow needles, which dissolve but sparingly in hot water, are nearly insoluble in cold water, but dissolve easily in alcohol and in ether. The salts of amidodinitrocresol are, for the most part, but slightly soluble.—The *magnesium-salt* is the most characteristic; it separates, on mixing concentrated solutions of the ammonium-salt and magnesium-sulphate, in small crystals, the solution of which in warm water yields the salt in needles an inch long. (Kellner and Beilstein, Ann. Ch. Pharm. cxxviii. 164.)

Methyltoluene, $C^8H^{10} = C^7H^7(CH^3) = C^6H^4(CH^3).CH^3$. (Glinzer and Fittig, *loc. cit.*)—This compound, isomeric with ethylbenzene or phenyl-ethyl (iv. 484), is prepared, similarly to the latter, by the action of sodium on a mixture of bromotoluene, methylic iodide, and ether, perfectly free from water and alcohol, and cooled with ice. It is a colourless mobile liquid, having a peculiar odour, not like that of benzene, a specific gravity of 0·8621 at 195°, and boiling at 139°—140° (six or seven degrees higher than ethylbenzene). It is probably identical with xylene from coal-tar oil, and forms with fuming sulphuric acid a sulpho-acid, whose barium-salt crystallises, like the xylene-sulphite, in spherical aggregations; the potassium-salt, $C^8H^9KSO^3$, forms silky laminæ.

By oxidation with *chromic acid*, methyltoluene (like xylene) yields terephthalic acid, $C^8H^6O^4$, whereas ethylbenzene yields benzoic acid.

Methyltoluene, warmed with fuming *nitric acid*, forms two isomeric dinitro-compounds, $C^8H^8(NO^2)^2$, one of which melts at 123·5°, and crystallises in long capillary needles; while the other, which melts at 93° (like dinitroxylene), forms large, colourless, monoclinic crystals. When methyltoluene is dropt into a mixture of 2 vols. nitric and 1 vol. fuming sulphuric acid, cooled at the commencement, trinitromethyltoluene, $C^8H^7(NO^2)^3$, is formed as a white precipitate, which separates from alcohol in rather large stellate crystals, melting at 137°.

Dioxymethyltoluene, $C^9H^{12}O^2 = C^7H^6(CH^3O)^2$.—Already described as methylate of benzylene (i. 577). When heated with acetic acid, it is converted into benzoic hydride and methylic acetate:

$$C^7H^6(CH^3O)^2 + 2(C^2H^3O.HO) = C^7H^6O + 2(C^2H^3O.CH^3O) + H^2O.$$

Hydrochloric acid likewise converts it into benzoic hydride. (Cannizzaro, Bull. Soc. Chim. [1866], ii. 216.)

Nitrotoluenes (i. 574).—*Mononitrotoluene*, $C^7H^7(NO^2)$, is there described as a liquid;

but, according to **Jaworsky** (Jahresb. 1865, p. 542), a purer product may be obtained by dissolving ordinary nitrotoluene in fuming sulphuric acid, and treating the product with water, whereupon nitrotoluene-sulphuric acid (p. 860) remains dissolved, and pure nitrotoluene is precipitated; also by redistilling the ordinary product of the action of nitric acid upon toluene, and collecting the portion which distils below 240°. It separates from alcohol, in white shining crystals, which melt at 54°, and distil without decomposition at 238°.

Chloronitrotoluene, $C^6H^3(NO^2)Cl.CH^3$, is formed by the action of fuming nitric acid upon chlorotoluene. The isomeric compound *nitrobenzylic chloride*, $C^6H^4(NO^2).CH^2Cl$, is formed in like manner from benzylic chloride. It crystallises from alcohol in fine colourless laminæ. Chromic acid converts it into nitrodracylic acid.

Benzylic chloride, treated with fuming nitric acid, likewise yields an oily liquid, slightly soluble in alcohol, which has not been much examined. This liquid, treated with chromic acid, also yields nitrodracylic acid. (**Beilstein** and **Geitner**, Bull. Soc. Chim. [1866], ii. 469.)

Trinitrotoluene, $C^7H^5(NO^2)^3$, is obtained by keeping toluene in a state of gentle ebullition with fuming nitric acid for several days, and precipitating with water. It forms white needles, which melt at 82°, are very slightly soluble in cold, easily soluble in boiling alcohol and in ether. It is isomeric with chrysanisic acid. (**Wilbrand**, Ann. Ch. Pharm. cxxviii. 178.)

Oxytolic Acid, $C^7H^6O^3$.—An acid isomeric with oxybenzoic and salicylic acids, produced by oxidising toluene with dilute nitric acid (iv. 321).

Sulphur-derivatives of Toluene, and Compounds isomeric with them.

Märcker (Ann. Ch. Pharm. cxxxvi. 79; Jahresb. 1865, p. 543) has obtained a toluenic sulphydrate analogous to cresol, and the isomeric compound, benzylic sulphydrate, analogous to benzylic alcohol; also toluenic disulphide, and the corresponding benzylic disulphide; and benzylic protosulphide, to which no corresponding toluene-compound has yet been produced.

Benzylic Sulphydrate, $C^7H^8S = \left.\begin{matrix}C^7H^7\\H\end{matrix}\right\}S = C^6H^5.CH^2(SH)$, is obtained by mixing an alcoholic solution of potassic sulphydrate (or sulphocarbonate) with chlorotoluene or bromotoluene (? benzylic chloride or bromide), adding water after 24 hours, and rectifying the oil thereby precipitated (**Märcker**, Ann. Ch. Pharm. cxxxvi. 75; Jahresb. 1865, p. 543). It is a colourless strongly refractive liquid, having a disagreeable alliaceous odour, and makes the eyes water. It has a specific gravity of 1·058 at 20°, and boils at 194°—195°. It decomposes *mercuric oxide*, forming the compound $C^{14}H^{14}Hg''S^2$, which crystallises from hot absolute alcohol in long needles.—With *mercuric chloride*, in alcoholic solution, it forms a precipitate containing $C^{14}H^{14}Hg''S^2.Hg''Cl^2$.—With *acetate of lead*, in alcoholic solution, it forms a crystalline precipitate of plumbobenzylic sulphydrate, $C^{14}H^{14}Pb''S$; with *silver-* and *cadmium-salts*, white precipitates; with *nickel-* and *copper-salts*, green precipitates; and with *iron-*, *cobalt-*, *platinum-*, and *gold-salts*, brown precipitates. Benzylic sulphydrate is converted, by exposure to the air, into benzylic sulphide (p. 859).

Toluenic or *Metabenzylic Sulphydrate*, $C^6H^4(SH).CH^3$. (**Märcker**, *loc. cit.*—**Jaworsky**, Jahresb. 1865, p. 542.)—This compound, isomeric with the preceding, is prepared by distilling toluene-sulphochloride, $C^7H^7SO^2Cl$ (p. 859), with zinc and dilute sulphuric acid. It then passes over with the vapour of water, while the less volatile toluenic sulphide remains behind. It crystallises very easily from ether, in large white laminæ, unctuous to the touch, and having a peculiar odour. It is very soluble in *ether*, sparingly soluble in *alcohol*, insoluble in *water*; melts at 42·5° to 43°, volatilises easily with vapour of water, and distils by itself without decomposition. The alcoholic solution becomes heated in contact with *mercuric oxide*, and forms the compound $C^{14}H^{14}Hg''S^2$, which crystallises in laminæ having a satiny lustre; with *mercuric chloride*, it forms the compound $C^{14}H^{14}Hg''S^2.Hg''Cl^2$.—*Lead-salts* throw down the compound $C^{14}H^{14}Pb''S^2$, in orange-yellow flocks.—*Silver-salts* form a siskin-green, *platinic chloride* an orange-yellow, *auric chloride* a light-green, *nickel-salts* a green, *copper-salts* a green, and *chloride of cobalt* a violet precipitate. Toluylenic sulphydrate dissolves in warm concentrated sulphuric acid, with evolution of sulphurous anhydride, forming a deep-blue solution, from which water throws down a reddish resinous body, redissolved with blue colour by sulphuric acid. Benzylic sulphydrate does not exhibit this reaction. (**Märcker**.)

Benzylic sulphydrate is oxidised by strong nitric acid, forming sulphuric acid, benzoic hydride, and small quantities of other products. Toluylenic sulphydrate, on the other hand, when added to nitric acid of specific gravity 1·3, is converted into toluylenic dioxysulphide, $C^{14}H^{4}O^{2}S^{2}$, while nitrotoluene-sulphuric acid remains in solution, (Märcker.)

Benzylic Sulphide, $(C^7H^7)^2S = \left.\begin{matrix}C^6H^5.CH^2\\ C^6H^5.CH^2\end{matrix}\right\}S$. (Märcker, *loc. cit.*).—This compound is produced by the action of an alcoholic solution of potassic monosulphide on chlorotoluene (more probably tolylic or benzylic chloride), and separates, on dilution with water, as an oily mass, which soon solidifies. It is insoluble in *water*, but dissolves easily in *alcohol* and *ether*, and crystallises, by slow evaporation of its solutions, in long needles by rapid cooling, in shining laminæ. It melts at 49°, volatilises without decomposition, and is not precipitated by metallic salts. When added to cooled *nitric acid* of specific gravity 1·3, it is converted into oily oxybenzylic sulphide, $(C^7H^7)^2SO$, which becomes crystalline on being mixed with water. Benzylic sulphide boiled with *nitric acid* of specific gravity 1·3, or treated with stronger acid, dissolves almost completely, with formation af sulphuric, benzoic, and nitrobenzoic acids, and a small quantity of a yellow acid, the barium-salt of which crystallises in yellow laminæ.

Benzylic sulphide, subjected to dry distillation, gives off a large quantity of sulphydric acid gas, and yields (at 200°) a distillate, consisting of toluene (boiling at 112°) and benzylic sulphydrate. Between 240° and 250°, tolylene, C^7H^6, passes over, solidifying in the crystalline form as it cools; and at still higher temperatures, the distillation being ultimately conducted in a current of air, two other crystalline bodies collect in the neck of the retort—viz., tolallylic sulphide, $(C^7H^5)^2S$ (p. 851), and a body consisting of $C^{28}H^{18}S$, which is insoluble in water, very sparingly soluble in absolute alcohol even at the boiling heat, more soluble in ether or benzene, and crystallises in long white needles; it melts at 180°, sublimes in needles or laminæ, and is, perhaps, identical with Laurent's thionessal (p. 779).

Benzylic Oxysulphide, $(C^7H^7)^2OS$, formed by the action of cooled nitric acid on benzylic sulphide, crystallises from hot water, or from alcohol, in laminæ having a satiny lustre, melts at 130°, and solidifies again at the same temperature. It dissolves readily also in ether, and melts under boiling water before dissolving. (Märcker.)

Benzylic Disulphide, $C^{14}H^{14}S^2 = \left.\begin{matrix}C^6H^5.CH^2\\ C^6H^5.CH^2\end{matrix}\right\}S^2$, is formed, as above mentioned, by the oxidation of benzylic sulphydrate in contact with the air, more quickly on evaporating a solution of the sulphydrate containing ammonia, or by the action of potassium-disulphide on chlorotoluene (benzylic chloride), in alcoholic solution. It crystallises in white shining laminæ, melts at 65° or 67°, dissolves easily in ether and in boiling alcohol, but not in water. It decomposes when heated, yielding the same compounds as the monosulphide, and is reconverted by nascent hydrogen into benzylic sulphydrate. It does not precipitate metallic salts. (Märcker.)

Toluenic or *Metabenzylic Disulphide,* $\left.\begin{matrix}C^6H^4(CH^3)\\ C^6H^4(CH^3)\end{matrix}\right\}S^2$, isomeric with the preceding, remains in the residue obtained in preparing toluenic sulphydrate from toluene-sulphochloride, and is likewise formed, on evaporating a solution of toluenic sulphydrate in alcoholic ammonia. It crystallises in large needles or laminæ, melts at 41°, is insoluble in water, but dissolves easily in hot alcohol, and especially in ether. By hydrogen it is reconverted into toluenic sulphydrate. (Märcker.)

Benzylic Dioxysulphide, $C^{14}H^{14}O^2S^2$, produced by the action of nitric acid on toluenic sulphydrate (p. 858), is insoluble in water and in aqueous potash, but dissolves in ether, alcohol, or benzene, and crystallises in large transparent prisms, which melt at 74°, solidify again at the same temperature, and when quickly heated, burn with brilliant scintillation. The alcoholic solution of this compound is not precipitated by mercuric chloride. (Märcker.)

TOLUENE-SULPHAMIDE. $C^7H^7.SO^2.NH^2$. Syn. with SULPHOTOLUOLAMIDE (p. 527).—Produced by the action of aqueous ammonia on toluene-sulphochloride or toluene-sulphobromide.

TOLUENE-SULPHOBROMIDE. $C^7H^7SO^2Br$. (Otto, Zeitschr. f. Chem. 1866, p. 657.—Otto and v. Gruber, *ibid.* 1867, p. 222.)—Produced by the action of bromine on toluene-sulphurous acid (p. 860) suspended in water. It forms long, oblique, rhombic prisms, insoluble in water, easily soluble in ether and in benzene, and melting at 95°—96°. By warm absolute alcohol, it is converted into ethylic toluene-sulphate; by potash into potassic toluene-sulphate; by ammonia into toluene-sulphamide.

TOLUENE-SULPHOCHLORIDE. $C^7H^7SO^2Cl$. (Fittig, Ann. Ch. Pharm. cvi. 280.—Märcker, *ibid.* cxxxvi. 79.—Jaworsky, Zeitschr. f. Chem. 1865, p. 221. —Otto, *ibid.* 1866, p. 657.)—Obtained by triturating toluene-sulphate of sodium with an equal weight of phosphoric pentachloride, and repeatedly washing the product with water. It is insoluble in water, but dissolves in alcohol, ether, and benzene, and separates from ether in beautiful rhombic plates, or sometimes in large prisms. It melts at 68°—69°, and boils, with almost complete decomposition, at 250°.

It is scarcely attacked by water in the cold, but is slowly decomposed on boiling, and quickly when heated with it in a sealed tube to a temperature above 100°, yielding hydrochloric and toluene-sulphuric acids. The same decomposition is produced by prolonged boiling with alkalis in aqueous solution, rapidly in alcoholic solution. The chloride acts gradually upon alcohol, even in the cold, forming ethyltoluene-sulphate. With aqueous ammonia and solid ammonium-carbonate, it easily forms toluene-sulphamide. When a solution of toluene-sulphochloride in pure and dry ether is treated with sodium-amalgam, toluene-sulphurous acid is produced. The chloride, treated with zinc and dilute sulphuric acid, yields toluene-sulphydrate.

Toluene-sulphochloride dissolves without alteration in a mixture of nitric and sulphuric acids, and is not attacked by strong nitric acid, even at the boiling heat. When distilled, it gives off sulphurous anhydride, and yields a liquid distillate, probably consisting of monochlorotoluene.

TOLUENE-SULPHURIC, TOLUOL-SULPHURIC, or **SULPHOTOLUIC ACID.** $C^7H^8SO^3 = C^7H^7.SO^3H = C^6H^4\left\{\begin{matrix}CH^3\\SO^3H\end{matrix}\right.$ (Deville, Ann. Ch. Pharm. xliv. 306.—Church, Jahresb. 1855, p. 634.—Fittig and Tollens, Ann. Ch. Pharm. cxxxi. 310.—Märcker, *ibid.* cxxxvi. 85.—Jaworsky, Zeitschr. f. Chem. 1865, p. 220.—Otto, *ibid.* 1866, p. 656.)—This acid, already partly described as BENZYLSULPHUROUS ACID (p. 553), was discovered by Deville, who obtained it by the action of fuming sulphuric acid on toluene from tolu-balsam. It was afterwards prepared in like manner by Church, though in an impure state, from the toluene of coal-tar; and by Fittig and Tollens from synthetically-formed methylbenzene or phenyl-methyl (iv. 486). Otto obtained it by oxidation of toluene-sulphurous acid, and Märcker produced it, together with nitrotoluene-sulphuric acid, by treating toluene-sulphydrate with nitric acid. A few of its salts have been examined by Jaworsky.

The *barium-salt*, $C^{14}H^{14}Ba''S^2O^6$, obtained by dissolving toluene in fuming sulphuric acid, neutralising with water after a few days, and saturating with carbonate of barium, forms crystals, permanent in the air, easily soluble in water and in alcohol.—The *lead-salt*, $C^{14}H^{14}Pb''S^2O^6$, usually forms nodular crystalline masses, but may be obtained, by slow evaporation, in needle-shaped crystals; it is easily soluble in water and in alcohol.

Ethylic toluene-sulphate, $C^7H^7.SO^3(C^2H^5)$, is easily produced by the action of toluene-sulphochloride or toluene-sulphobromide on alcohol. It is insoluble in water, but soluble in alcohol and ether, and crystallises in fine thick prisms, which melt at 32°.

Amidotoluene-sulphuric Acid, $C^7H^6(NH^2).SO^3H$. Syn. with SULPHOTOLYLAMIC or BENZYLSULPHAMIC ACID. (See SULPHUROUS ETHERS, p. 527.)

Nitrotoluene-sulphuric Acid, $C^7H^6(NO^2).SO^3H = C^6H^4(NO^2)\left\{\begin{matrix}CH^3\\SO^3H\end{matrix}\right.$—There appear to be two modifications of this acid, the one produced from nitrotoluene by the action of fuming sulphuric acid, the other by that of nitric acid on toluene-sulphydrate, being evidently formed by the nitration of toluene-sulphuric acid. But the two acids have not been sufficiently examined to render their separate existence a matter of certainty.

Nitrotoluene-sulphuric acid is produced by treating toluene-sulphydrate with nitric acid, of specific gravity 1·3, and remains in solution, while toluene-disulphide crystallises out (p. 859). By evaporating the solution, it is obtained in deliquescent crystals.—Its *barium-salt*, $[C^7H^6(NO^2)SO^3]^2Ba''.2H^2O$, forms colourless, transparent, four-sided tablets, which dissolve easily in hot, slightly in cold water, are insoluble in alcohol, and give off their water of crystallisation at 110°.—The *lead-salt*, $[C^7H^6(NO^2)SO^3]^2Pb''.4H^2O$, forms transparent, very bulky, crystalline laminæ. (Märcker.)

Paranitrotoluene-sulphuric acid is produced by gently heating nitrotoluene with fuming sulphuric acid. Its barium-salt forms shining pale-yellow crystals, which contain $[C^7H^6(NO^2)SO^3]^2Ba''.3H^2O$, and give off their water at 110°. (Church; Jaworsky.)

TOLUENE-SULPHUROUS ACID. $C^7H^7.SO^2H = C^6H^4\left\{\begin{matrix}CH^3\\SO^2H\end{matrix}\right.$— *Tolylsulphurous* or *Benzylsulphurous Hydride*. (Otto, Zeitschr. f. Chem. 1866, p. 655.)—This acid is obtained, similarly to the homologous compound benzene-sulphurous acid or phenylsulphurous hydride (p. 564), by treating toluene-sulphochloride, dissolved in ether free from water and alcohol, with sodium-amalgam, and decomposing the resulting sodium-salt with hydrochloric acid. [At the same time there is formed a secondary product, having the empirical formula $C^9H^{10}SO^2$, which dissolves in hot alcohol, and crystallises therefrom in oblique rhombic prisms, melting at 75°—76°.]

Toluene-sulphurous acid crystallises from water in rhombic tables, unctuous to the touch, and having a brilliant satiny lustre; or from dilute solutions in long needles united in large tufts. It melts at 85°, dissolves sparingly in cold water, easily in boiling water—also in alcohol, ether, and benzene.

It is easily converted by oxidation into toluene-sulphuric acid, this effect being produed even by the oxygen of the air, though not so quickly as with benzene-sulphurous acid. When immersed in water, and subjected to the action of chlorine (best at a moderate heat), it is converted into toluene-sulphochloride, hydrochloric acid being formed at the same time. With bromine, in like manner, it yields hydrochloric acid and toluene-sulphobromide.

Toluene-sulphites.—The *barium-salt*, $(C^7H^7SO^2)^2Ba''$, is anhydrous, and crystallises in small shining laminæ, slightly soluble in cold water, more soluble in hot water and in ether.—The *calcium-salt*, $(C^7H^7SO^2)^2Ca''.8H^2O$, resembles the barium-salt in form and solubility.—The *silver-salt*, $C^7H^7SO^2Ag$, forms anhydrous iridescent laminæ, somewhat soluble in boiling water.

Ethylic toluene-sulphite, $C^7H^7.SO^2(C^2H^5)$, is easily produced by heating the acid with alcohol containing hydrochloric acid. It is liquid, insoluble in water, easily soluble in alcohol and ether.

TOLUENYL. Syn. with Tolyl or Benzyl.

TOLU-EUGENYL. Syn. with Eugeno-toluic Anhydride (ii. 605).

TOLUGLYCIC ACID. Syn. with Toluric Acid.

TOLUIC ACID. $C^8H^8O^2 = \left.\begin{matrix}C^8H^7O\\H\end{matrix}\right\}O = C^6H^5.CH^2.CO^2H$ (Kekulé).

Toluolic Acid. Toluylic Acid. (Noad [1847], Phil. Mag. [3], xxxii. 19.—Kraut, *Dissertation über Cuminol und Cymen* [Göttingen, 1854], p. 20.—Cahours, Ann. Ch. Pharm. cviii. 315.—Cannizzaro, *ibid.* xcvi. 246; cxix. 253; cxxiv. 252; Jahresb. 1861, p. 421; 1862, p. 267.—Möller and Strecker, Ann. Ch. Pharm. ciii. 64.—Temple, *ibid.* cxv. 277.—Griess, *ibid.* cxvii. 61.—Beilstein and Yssel de Schepper, *ibid.* cxxxvii. 301; Bull. Soc. Chim. 1866, i. 286.—Kekulé, *ibid.* 1866, ii. 46.)—An aromatic acid, homologous with benzoic acid, and isomeric with anisylous acid and methylic benzoate. It is produced: 1. By the action of dilute nitric acid on cymene (Noad), or xylene (Beilstein):

$$\underset{\text{Cymene.}}{C^{10}H^{14}} + O^6 = \underset{\substack{\text{Toluic}\\\text{acid.}}}{C^8H^8O^2} + \underset{\substack{\text{Oxalic}\\\text{acid.}}}{C^2H^2O^4} + 2H^2O.$$

$$\underset{\text{Xylene.}}{C^8H^{10}} + O^3 = \underset{\substack{\text{Toluic}\\\text{acid.}}}{C^8H^8O^2} + H^2O.$$

2. Synthetically by the action of sodium and carbonic anhydride on bromotoluene (Kekulé):

$$\underset{\substack{\text{Bromoto-}\\\text{luene.}}}{C^7H^7Br} + Na^2 + CO^2 = NaBr + \underset{\substack{\text{Toluate of so-}\\\text{dium.}}}{C^7H^7.CO^2Na}.$$

The toluic acid obtained by either of these three processes exhibits exactly the same properties, and is the true homologue of benzoic acid. A modification, called alpha-toluic acid, differing from toluic acid in some of its properties, but agreeing with it in composition, and in the essential character of being resolved by heat into toluene and carbonic anhydride, ($C^8H^8O^2 = C^7H^8 + CO^2$), is produced by boiling vulpic acid or cyanide of benzyl with alkalis (Cannizzaro). Another modification, obtained by Griess, by the action of nitrous acid on an alcoholic solution of amidotoluic or oxytoluamic acid (iv. 321), has been regarded as homologous with salylic acid; but as this acid has lately been shown to be identical with benzoic acid (p. 185), it is probable that the toluic acid obtained by the last-mentioned process is likewise identical with ordinary toluic acid.

Preparation of Toluic Acid.—1. From cymene.—One pt. of cymene is distilled in a capacious retort with 4 pts. of a mixture of common nitric acid with six times its volume of water, the distillate being repeatedly poured back into the retort. The reaction takes place quietly, the oil first becoming blue, then dark-yellow, then viscid, and finally sinking to the bottom. The operation is finished when the drops of oil, which at first float upon the distillate, are replaced by white crystals, and on cooling the retort becomes filled with these crystals (Noad). If this method (which requires continuous boiling for a week) is exactly followed, and the toluic acid, as it is formed, is removed, so as to prevent any further action of the nitric acid, the acid is obtained perfectly pure (Kraut).—The toluic acid is the purer the weaker the nitric acid, and the more slowly the distillation is conducted; stronger acid acts violently, and forms nitrotoluic acid, which is difficult to separate. In order to effect the separation, the mixture is first freed from nitric acid and a yellow resin, by boiling with milk of lime; the filtered solution of the calcium-salt is then precipitated by hydrochloric or nitric acid; the precipitated acids are dissolved in baryta-water, and evaporated on a water-bath; the residue is treated with water; the solution filtered from the nitrotoluate of barium, which is difficultly soluble, is next evaporated, again treated with cold water, and filtered; and this treatment is repeated till no more nitrotoluate of barium separates out; the liquid is then precipitated by an acid, and the product is recrystallised. (Noad.)

2. From xylene.—The hydrocarbon is oxidised, as in the preceding process, with nitric acid diluted with five or six times its bulk of water, and the product is freed from the small quantity of nitrotoluic acid, formed at the same time, by distillation and treatment with sulphide of ammonium. (Beilstein and De Schepper.)

3. From toluene.—Bromotoluene, mixed with toluene, is introduced into a long-necked flask, provided with an upright condensing-tube; sodium, in quantity rather greater than that required by theory, is added in small pieces; the whole is heated in a water-bath; and a stream of carbonic anhydride is passed into the vessel for 24 to 48 hours. The sodium soon becomes covered with a blue crust, and is converted into a pasty mass of the same colour. As soon as the reaction is finished, the product is treated with water; the solution is filtered, to separate oily matters, consisting of unaltered toluene and bromotoluene, together with secondary products; and the filtered solution of sodium-toluate is acidulated with hydrochloric acid, to precipitate the toluic acid. (Kekulé.)

Properties.—Toluic acid is precipitated from the solutions of its alkaline salts by acids, as a white curdy mass, which appears crystalline under the microscope. It is very soluble in boiling water, and crystallises therefrom in needles on cooling. It dissolves very readily also in alcohol and ether. When pure, it is tasteless and inodorous. It melts at a temperature above 100° (at 175° to 175·5°, according to Kekulé), and sublimes, without decomposition, in fine needles.

Decompositions.—Toluic acid, heated with *lime* or *baryta*, is resolved into toluene and carbonic anhydride: $C^8H^8O^2 = C^7H^8 + CO^2$.—When boiled for some time with strong *nitric acid*, it is converted into nitrotoluic acid.—By distillation with *pentachloride of phosphorus*, it yields toluic chloride, C^8H^7OCl (Cahours).—When introduced into the animal organism, it passes into the urine as toluric acid (p. 868).

A mixture of toluate and formate of calcium yields by distillation, toluic aldehyde, C^8H^8O (Cannizzaro, p. 864):

$$\underset{\substack{\text{Toluate of}\\\text{calcium.}}}{C^{16}H^{14}Ca''O^4} + \underset{\substack{\text{Formate of}\\\text{calcium.}}}{C^2H^2Ca''O^4} = \underset{\substack{\text{Toluylic}\\\text{aldehyde.}}}{2C^8H^8O} + 2Ca''CO^3.$$

Toluates.—Toluic acid is monobasic, and its salts are mostly crystalline; they have not, however, been much examined.—The *ammonium-salt* forms small prisms.—The *barium-salt*, $C^{16}H^{14}Ba''O^4$, obtained by neutralisation, forms confused crystals.—The *calcium-salt*, $C^{16}H^{14}Ca''O^4$, separates from its concentrated aqueous solution in long shining needles.—The *cupric salt*, $C^{16}H^{14}Cu''O^4$, is deposited, on mixing the potassium-salt with cupric sulphate, as a blue precipitate, slightly soluble in water.—The *potassium-salt*, obtained by neutralisation, forms long shining needles.—The *silver-salt*, $C^8H^7AgO^2$, is obtained, by double decomposition, as a curdy precipitate, crystallising from hot water in small needles.—The *sodium-salt* is more soluble than the potassium-salt, and does not crystallise.

Derivatives of Toluic Acid.

IODOTOLUIC ACID, $C^8H^7IO^2$.—Produced by the action of hydriodic acid on diazotolu-oxytoluamic acid (iv. 322). It forms white laminæ or needles, slightly soluble in water, freely in alcohol or ether. (Griess.)

NITROTOLUIC ACID, $C^8H^7(NO^2)O^2$.—This acid is easily produced by boiling toluic acid with strong nitric acid. It may also be prepared directly from cymene, by boiling that hydrocarbon with the strongest fuming nitric acid, as long as red fumes are evolved. The residue deposits a large quantity of crystals on cooling, and gives a considerable precipitate when treated with water; the whole mass is then washed on a filter with cold water, then digested with ammonia and filtered, whereby a little oily matter is separated. The filtrate is decomposed with hydrochloric acid; the precipitated nitrotoluic acid is washed with water, dried, dissolved in hot alcohol, and boiled with animal charcoal; and the filtrate is left to evaporate.

Nitrotoluic acid forms beautiful pale-yellow rhombic prisms, slightly soluble in cold water, soluble in hot alcohol.

Nitrotoluate of Ammonium forms long needles; it easily gives up part of its ammonia, and the whole when boiled with animal charcoal.—The *barium-salt*, $C^{16}H^{12}Ba''(NO^2)^2O^4$, is thrown down, on mixing the ammonium-salt with chloride of barium, as a white curdy precipitate, which dissolves abundantly in hot water, and separates in stellate groups of needles on cooling.—The *calcium-salt*, $C^{16}H^{12}Ca''(NO^2)^2O^4$, is obtained in like manner as a crystalline precipitate, more soluble in water than the barium-salt, and crystallising therefrom in oblique rhombic prisms.—*Cupric salt.* Cupric sulphate forms, with the perfectly neutral ammonium-salt, a precipitate consisting of a basic salt.—The *potassium-salt* is very soluble, and crystallises with difficulty in small needles.—The *silver-salt*, $C^8H^6Ag(NO^2)O^2$, is a white curdy precipitate, very much like chloride of silver, very soluble in boiling water (blackening if too long boiled), from which it separates in feathery crystals on cooling; slightly soluble in alcohol.—The *sodium-salt* is uncrystallisable.—The *strontium-salt* is very much like the barium-salt, excepting that the crystals are larger, and more soluble in water. (Noad.)

Nitrotoluic Ethers.—The *ethylic ether*, $C^8H^6(C^2H^5)(NO^2)O^2$, is prepared by distilling the alcoholic solution of the acid saturated with hydrochloric acid gas, till the mixture of hydrochloric acid and alcohol begins to show turbidity with water; the oil remaining in the retort then solidifies to a crystalline mass, which, after being washed with carbonate of potassium and with water, is dried between blotting-paper. The ether melts in the water-bath, and forms a clear liquid, which, on cooling, solidifies to a radiated crystalline mass. It has a pleasant odour. It is decomposed by potash into alcohol and toluic acid; does not form an amide with ammonia. (Noad.)

Methylic Nitrotoluate, $C^8H^6(CH^3)(NO^2)O^2$, is prepared like the ethyl-compound; but, as it is generally contaminated with black greasy secondary products, it must be dissolved in strong nitric acid, boiled therewith for a short time, and precipitated by water; it then falls down in oily drops, which soon solidify in the crystalline state. It may be completely purified by distillation with water, and is then quite colourless. It dissolves easily in ether, and is resolved by potash into nitrotoluic acid and methylic alcohol. (Noad.)

DINITROTOLUIC ACID, $C^8H^6(NO^2)^2O^2$.—This acid is obtained by digesting nitrotoluic acid, for two days, with a mixture of equal parts of fuming nitric and fuming sulphuric acid; and is precipitated from the solution by water, in crystals, which may be purified by recrystallisation from boiling water.—The *silver-salt*, $C^8H^5Ag(NO^2)^2O^2$, is a white precipitate. (Temple, Ann. Ch. Pharm. cxv. 277.)

OXYTOLUAMIC ACID, $\left.\begin{matrix}H^2\\(C^8H^6O)\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$ or AMIDOTOLUIC ACID, $C^8H^7(NH^2)O^2$, has been already described (iv. 321).

Diazotolu-oxytoluamic Acid, $C^8H^6N^2O^2.C^8H^9NO^2$ (iv. 322).

Appendix to Toluic Acid.

Alphatoluic Acid, $C^8H^8O^2$. (Cannizzaro, Ann. Ch. Pharm. xcvi. 216; further, Compt. rend. lii. 966; liv. 1225; Jahresb. 1861, p. 421; 1862, p. 267.—Möller and Strecker, Ann. Ch. Pharm. cxiii. 64.)—Cannizzaro found, in 1855, that by boiling cyanide of benzyl (i. 573), with potash-ley, an acid is obtained having the composition of toluic acid, but melting below 100°. Möller and Strecker, in 1857, by boiling vulpic acid with baryta-water, also obtained an isomer of toluic acid, which they denominated alphatoluic acid; and Cannizzaro subsequently found that this acid was identical with that which he had obtained from benzylic cyanide.

Preparation.—Benzylic cyanide (i. 573) is boiled with strong potash-ley till the whole is dissolved, and no more ammonia is given off; the liquid is then diluted with water, and the concentrated filtrate precipitated with hydrochloric acid (Cannizzaro).—2. Vulpic acid is boiled for several hours with a solution of barium-hydrate, saturated while warm (potash or soda would produce oxotolylic acid, iv. 217), till the liquid has become colourless; the solution is then filtered, to separate oxalate of barium; and the filtrate is supersaturated with hydrochloric acid, which, as the liquid cools, throws down the greater part of the alphatoluic acid as a crystalline precipitate. The filtered solution, when evaporated, deposits a small additional quantity of the same acid, together with a large quantity of barium-chloride.

Alphatoluic acid, purified by recrystallisation from boiling water, forms broad, thin, colourless, shining laminæ, having the form of acute rhombs, very much like benzoic acid. It has an odour like that of the perspiration of horses. It melts at 76·5°, and gives off (even below 100°), vapours which excite coughing. It boils without decomposition at 265·5° (corrected; the temperature directly observed was 262°). The specific gravity of the solid acid is nearly 1·3; that of the fused acid, compared with water at

[illegible]

Parachlorotoluic Acid. [illegible] in water.

TOLUIC ALDEHYDE. [illegible] With alcoholic potash it forms [illegible]

$$[illegible] = [illegible] + C^8H^{10}O.$$

TOLUIC ANHYDRIDE. [illegible] known.—*Salicylotoluic Anhy*- [illegible] is formed by heating dry salicylate of sodium with [illegible] the product with a mixture of [illegible] the ethereal solution to evaporate [illegible]

TOLUIC CHLORIDE. [illegible] —Formed by distilling toluic acid with [illegible] liquid, of specific gravity [illegible] Fumes in [illegible] with water, alcohol, and [illegible] Heated with salicylic [illegible] it yields [illegible] it yields eugenotoluic anhy- [illegible]

TOLUIC ETHERS. *Ethylic toluate*, [illegible] is obtained by passing [illegible] distilling to about two- [illegible] It is then precipitated as a heavy [illegible] dried over chloride of calcium, [illegible] smelling like benzoic ether, having a [illegible] 228° [illegible]

Ph[illegible] is obtained by distilling salicylotoluic anhydride [illegible] and may be purified by boiling for a short time with weak [illegible] recrystallisation from ether-alcohol. It forms white [illegible] melting at 71° to 72°, and smelling like geraniums when heated. (Kraut.)

TOLUIDENE, or **BENZYLIDENE.** [illegible]—An aldehyde-radicle, related to [illegible] or benzylene (p. 577) in the same manner as ethylidene to ethylene.—The *Bromide*, $C^7H^6Br^2$, is formed by the action of phosphoric pentabromide on bitter-almond-oil, C^7H^6O (p. 853).

By heating toluidine, rosaniline, and other bases with bitter-almond-oil, compounds are obtained, derived from the original compound by substitution of 1 at. toluidene for 2 at. hydrogen.

Benzylidene-rosaniline, $\left.\begin{matrix}(C^6H^6)''\\(C^{20}H^{16})^{vi}\\H\end{matrix}\right\}N^3$, is a copper-coloured, crystalline, feebly basic compound, obtained by heating rosaniline with bitter-almond-oil to 100° or 120° (Schiff, Compt. rend. lxv. 45). The other substitution-products, just mentioned, will be described under TOLUIDINE (p. 867) and TOLYLENE-DIAMINE (p. 872).

TOLUIDES. Compounds homologous with the anilides (iv. 419), derived from toluidine-salts by abstraction of water, or from toluidine by substitution of an acid-radicle for hydrogen, and produced in many instances by heating toluidine with acids; *e.g.*:

$$\underset{\text{Acetic acid.}}{C^2H^3O.H.O} + \underset{\text{Toluidine.}}{C^7H^7.NH^2} - H^2O = \underset{\text{Acetotoluide.}}{C^7H^6(C^2H^3O).NH^2}.$$

They may be regarded as amides containing the radicle tolyl or benzyl; *e.g.*, acetotoluide = tolylacetamide, $\left.\begin{matrix}C^2H^3O\\C^7H^7\\H\end{matrix}\right\}N$. See TOLYLACETAMIDE, TOLYLBENZAMIDE, &c. (pp. 871, 872).

TOLUIDINE. $C^7H^9N^2$ = *Amidotoluene*, $C^7H^7(NH^2)$.—A crystalline base, produced by the reducing action of sulphydric acid or ferrous acetate on nitrotoluene. It has been already described as BENZYLAMINE (i. 575); but Cannizzaro has shown that a base having the same composition but different properties, is formed by the action of alcoholic ammonia on benzylic chloride (p. 867). The compound thus formed is a true ammonia-base or amine, and is properly designated as benzylamine or tolylamine, and represented by the formula $\left.\begin{matrix}C^7H^7\\H^2\end{matrix}\right\}N$; whereas the base obtained by reduction of nitrotoluene is rather to be regarded as amidotoluene or toluidine, $C^7H^7(NH^2)$.

Preparation. (See i. 575).—For preparing toluidine on the large scale, Hugo Müller (Zeitschr. f. Chem. 1864, p. 161; Jahresb. 1864, p. 423) converts commercial toluene, boiling at 108° to 114° (pure toluene boils at 111°), into nitrotoluene, by pouring a mixture of nitric and sulphuric acids into it in a slow stream (if the action becomes too rapid, dinitrotoluene is also formed), and reduces this product with iron and acetic acid. The crystalline toluidine thus obtained is freed from adhering liquid base by drenching it with the portion of American petroleum or Burmese naphtha, which boils between 80° and 100° (chiefly heptylic hydride), and finally recrystallising it from this hydrocarbon. E. Sell (Chem. Soc. J. xvi. 186) prepares toluidine, in considerable quantity, from that portion of the residue of the aniline manufacture (*queues d'aniline*), which boils below 270° (the higher portions containing paraniline, &c., iv. 352). This liquid is distilled in a large copper retort provided with a long condensing-tube not cooled; the portion of the distillate boiling between 180° and 230° is subjected to fractional distillation; the several portions of the distillate are treated with a hot solution of oxalic acid; and the sparingly soluble oxalate of toluidine is decomposed by potash-ley as soon as a sample of the base separated by ammonia solidifies at once. The brown toluidine thus separated, which crystallises on cooling, is washed with water, pressed between paper, and distilled. It passes over between 198° and 200°, and solidifies in the receiver in snow-white crystals, which gradually turn brown in contact with the air. (Sell.)

Toluidine boils at 205°—206°, under a pressure of 730 mm. (Städeler, J. pr. Chem. xcvi. 65.)

Reactions.—Toluidine is absolutely incapable of neutralising dilute sulphuric acid (Wacklyn, *Laboratory*, i. 3). When moderately heated with *fuming sulphuric acid*, it forms tolylsulphamic or sulphotolylamic acid, $C^7H^9NSO^3$ (p. 527; Sell, *loc. cit.*).—An aqueous solution of sulphate of toluidine mixed with *cyanate of potassium*, deposits white needles of monotolylcarbamide, $\left.\begin{matrix}(CO)''\\C^7H^7\\H^3\end{matrix}\right\}N^2$ (Sell). Finely-divided toluidine combines rapidly with *ethylic cyanate*, forming tolyl-ethylcarbamide. $\left.\begin{matrix}(CO)''\\C^7H^7\\C^2H^5\\H^2\end{matrix}\right\}N^2$. (Sell.)

An alcoholic solution of toluidine, heated (not above 80°) with an equal volume of *carbonic disulphide*, forms ditolylsulphocarbamide, $\left.\begin{matrix}(CS)''\\(C^7H^7)^2\\H^2\end{matrix}\right\}N^2$. (Sell.)

Toluidine, fused with an equal weight of *succinic acid*, forms tolylsuccinimide, $\left.\begin{matrix}(C^4H^4O^2)''\\C^7H^7\end{matrix}\right\}N$, and ditolylsuccinamide, $\left.\begin{matrix}(C^4H^4O^2)''\\(C^7H^7)^2\\H^2\end{matrix}\right\}N^2$. (Sell.)

A mixture of toluidine and *acetic acid*, treated with *trichloride of phosphorus*, yields ethenyl-ditoluidine,* $C^{16}H^{18}N^2$ (Hofmann; see p. 867).—With *benzoic hydride* (bitter-almond-oil), toluidine forms dibenzylidene-tolylamine, $C^{14}H^{26}N^2 = N^2(\overset{''}{C^7H^6})^2(C^7H^7)^2$ (Schiff, Jahresb. xviii. 429).—With *quinone* and *perchloroquinone*, toluidine forms compounds homologous with those produced by aniline (Hofmann, iv. 426).—A mixture of 1 at. hydrochlorate of toluidine and 1 at. *azobenzene* is converted (at 230°) into a black mass, containing, together with unaltered toluidine, a ruby-red colouring-matter soluble in hot water, a violet substance somewhat less soluble in water, and a blue substance soluble in alcohol.—With *nitrobenzene*, in like manner, a tarry greenish mass is formed, which does not contain any colouring-matters (Städeler, Jahresb. 1865, p. 409).—Toluidine heated with half its weight of *acetate of rosaniline*, forms tritolyl-rosaniline or toluidine-blue, $C^{20}H^{16}(C^7H^7)^3N^3$. (Hofmann, iv. 472.)

Cyanotoluidine, $C^8H^9N^2$ (i. 576), is resolved, by evaporation of its hydrochlorate, similarly to cyaniline (iv. 443), into sal-ammoniac, hydrochlorate of toluidine, oxamide, monotolyloxamide, and ditolyloxamide. (Sell.)

Derivatives of Toluidine containing Alcohol-radicles.

PHENYLTOLUIDINE, $C^{13}H^{13}N = C^7H^6(C^6H^5).NH^2$.—This base, which Hofmann obtained by the dry distillation of a salt of tritolyl-rosaniline (iv. 472), is likewise produced, together with diphenylamine and ditolylamine, by heating hydrochlorate of toluidine with aniline, or hydrochlorate of aniline with toluidine. The three bases may be separated by fractional distillation, but the separation is difficult, as their boiling-points do not differ by more than 25° or 30°. Phenyltoluidine boils at about 330°. (De Laire, Girard, and Chapoteaut, Bull. Soc. Chim. 1866, *ii. 360.*)

BENZYLTOLUIDINE, or TOLYLTOLUIDINE, $C^{14}H^{15}N = C^7H^6(C^7H^7).NH^2$. *Ditolylamine.*—Produced by heating 1 at. hydrochlorate of toluidine with 1½ at. of the free base, to 210°—240°, in a long-necked flask provided with a condensing-tube, or more quickly by heating the mixture in a sealed tube under a pressure of four or five atmospheres. On treating the product with hydrochloric acid diluted with twenty or thirty times its bulk of water, the hydrochlorate of benzyltoluidine is decomposed by the water; and the benzyltoluidine thus separated, floats on the surface as an oil which solidifies on cooling, and may be purified by recrystallisation. It boils between 355° and 360°. It forms unstable salts, which are decomposed by water. Nitric acid turns it yellow, a character by which it is distinguished from diphenylamine. (De Laire, Girard, and Chapoteaut, *loc. cit.*)

DIBENZYLTOLUIDINE, $C^{21}H^{21}N = C^7H^5(C^7H^7)^2.NH^2$.—This base, isomeric with tribenzylamine, $(C^7H^7)H^3N$ (i. 576), is produced by heating an alcoholic solution of 1 at. toluidine with 2 at. benzylic chloride, and subjecting the base, separated from the product by potash, to a repetition of the same treatment. It crystallises in slender needles, melting between 54·5° and 55° (tribenzylamine crystallises in small tables, and melts at about 93°). It is insoluble in water, slightly soluble in cold, easily in hot alcohol, and becomes yellowish on exposure to light.—The *hydrochlorate* dissolves readily in alcohol, and is decomposed by water, with separation of the base.—The *chloroplatinate*, which is also decomposed by water, crystallises from an alcoholic solution mixed with ether. (Cannizzaro.)

Derivatives of Toluidine containing Aldehyde-radicles.

These compounds are formed by the action of aldehydes on toluidine.—*Diethylidene-ditoluidine*, $C^{18}H^{22}N^2 = C^{14}H^{10}(\overset{''}{C^2H^4})^2.(NH^2)^2 = (\overset{''}{C^2H^4})^2.(C^7H^7)^2N^2$, obtained by the action of acetic aldehyde on toluidine, crystallises in yellow nodules, and forms red resinous salts with acids.—*Diallylidene-ditoluidine*, $(\overset{''}{C^3H^4})^2(C^7H^7)^2N^2$, is obtained in like manner with acrolein, as a brown resinous mass.—*Dibenzylidene-ditoluidine*,

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* Ethenyl, C^2H^3, is the triatomic radicle commonly called *Vinyl*. For Hofmann's systematic nomenclature of hydrocarbons, see Proc. Roy. Soc. xv. 55.

$C^{28}H^{26}N^2 = (C^7H^6)^2(C^7H^7)^2N^2$, produced by the action of bitter-almond-oil on toluidine, separates from alcohol as a yellow, crystalline, indifferent body, which melts in boiling water, and is converted, at 160°, into yellow needles, melting at 120°—125°, and capable of combining with acids and chlorides. (Schiff, Zeitschr. f. Chem. 1865, p. 400.)

Ethenyl-ditoluidine, $C^{16}H^{18}N^2 = C^{14}H^{11}(C^2H^3)'''.(NH^2)^2$. (Hofmann, Proc. Roy. Soc. xv. 55; Jahresb. 1865, p. 415.)—This base, derived from 2 at. toluidine by substitution of the triatomic radicle ethenyl (vinyl) for 3 at. hydrogen, is produced by the action of trichloride of phosphorus and chloride of acetyl on toluidine at 160°:

$$6C^7H^9N + 3C^2H^3OCl + PCl^3 = 3C^{16}H^{18}N^2 + PH^3O^3 + 6HCl.$$

When purified by recrystallisation from alcohol, it forms white laminæ, resembling the corresponding phenyl-compounds.

Azotoluidines.

Azotoluidine, or Diazotoluene, $C^7H^6N^2 = C^7H^4N'''.NH^2$. (Griess, Chem. Soc. J. xx. 86.)—The salts of this base (which has not been obtained in the free state) exhibit considerable analogy, in their properties and modes of formation, to the corresponding aniline-derivatives (iv. 430); they appear, however, to be somewhat more stable, and to crystallise more readily.

The *nitrate*, $C^7H^6N^2.NHO^3$, is best prepared by the action of nitrous acid on an aqueous solution of nitrate of toluidine, but it may also be formed from azoditoluidine. It forms long white needles, which are decomposed on boiling with water, according to the equation:

$$\underset{\text{Nitrate of Azotoluidine.}}{C^7H^6N^2.NHO^3} + H^2O = \underset{\text{Cresol.}}{C^7H^8O} + NHO^3 + N^2.$$

The other salts are obtained from the nitrate in the same manner as the corresponding phenyl-compounds.—The *chloroplatinate*, $2(C^7H^6N^2.HCl).PtCl^4$, is precipitated, in fine yellow prisms, on adding platinic chloride to a dilute solution of the hydrochlorate. When ignited with soda, it yields an aromatic oil, having the composition of chlorotoluene, C^7H^7Cl.

The *sulphate*, $C^7H^6N^2.SH^2O^4$, is obtained in brilliant plates, needles, or prisms, according to the circumstances under which it crystallises. When heated with strong sulphuric acid, it gives off the whole of its nitrogen, and is converted into disulphotolylenic acid, $C^7H^{10}S^2O^8 = C^7H^6.2SH^2O^4$, the barium-salt of which, $C^7H^6Ba''S^2O^8$, crystallises in long white needles.—The *perbromide*, $C^7H^6N^2.HBr^3$, is precipitated by bromine-water from aqueous nitrate of azotoluidine, as a yellow oil, which, after evaporation of the excess of bromine, solidifies to a crystalline mass.

Azoditoluidine, $C^{14}H^{15}N^3 = C^{14}H^{11}N'''.(NH^2)^2$, or Diazotoluene-amidotoluene, $\left\{\begin{matrix}C^7H^6N^2\\C^7H^7(NH^2)\end{matrix}\right.$.—This base is produced by passing nitrous acid vapour through a solution of toluidine in a small quantity of strong alcohol mixed with two or three times its volume of ether, till a drop of the solution leaves, on evaporation, a residue of yellow needles. The solution of these crystals, left to evaporate, deposits the base in yellow needles, which must be washed with alcohol, and recrystallised from a mixture of alcohol and ether. The crystals have a strong lustre, and correspond, in solubility and other properties, with azodiphenyl-diamine (iv. 459).

The *chloroplatinate*, $C^{14}H^{15}N^3.2HCl.PtCl^4$, is obtained in glittering plates, resembling iodide of lead, on mixing an alcoholic solution of the base with platinic chloride; it deflagrates at a high temperature. (Griess, Chem. Soc. J. xix. 67.)

Azophenyltoluidine, $C^{13}H^{13}N^3 = C^{13}H^9N'''.(NH^2)^2$, or Diazotoluene-amidobenzene, $\left.\begin{matrix}C^7H^6N^2\\C^6H^5(NH^2)\end{matrix}\right\}$, obtained by the action of aniline on nitrate of azotoluidine, crystallises in beautiful long yellow needles. (Griess, Chem. Soc. J. xx. 87.)

Appendix to Toluidine.

Benzylamine, $C^7H^9N = \left.\begin{matrix}C^7H^7\\H\end{matrix}\right\}N$. (Cannizzaro, Bull. Soc. Chim. 1864, ii. 126; 1865, ii. 218.)—This base, isomeric with toluidine, is formed, together with tribenzylamine, $(C^7H^7)^3N$ (i. 574), and probably also with dibenzylamine, $(C^7H^7)^2HN$, by the action of alcoholic ammonia on benzylic chloride, C^7H^7Cl. The mixture, after a few days, deposits tabular crystals of tribenzylamine, and on evaporating the filtered liquid in the water-bath, and treating the residue with hot water, a further portion of tribenzylamine remains undissolved, and the solution contains, together with sal-ammoniac, the hydrochlorate of benzylamine, and probably also of dibenzylamine. The hydrochlorate of benzylamine is separated from the more soluble portion by fractional crystallisation; and the free base separated from this salt by potash is dissolved in ether, freed from ether by evaporation, dehydrated by fused potash out of contact with the air, and then distilled—the portion which gives over at 182° being collected apart. For complete purification, it is converted into the solid carbonate by exposure to a stream of dry carbonic anhydride; the carbonate is washed with anhydrous ether, and dissolved in hydrochloric acid; and the crystallised hydrochlorate is decomposed with potash as above.

Benzylamine, thus prepared, is a colourless liquid, not altered by light, and boiling at 182°—183°. (Toluidine, described, at vol. i. p. 575, as benzylamine, is crystalline at ordinary temperatures, and melts at [illegible]°). It mixes with water in all proportions (toluidine is but slightly soluble in cold water), and is separated therefrom by potash, with faint yellowish colour. It absorbs carbonic anhydride rapidly, forming a crystalline compound; has a strong alkaline reaction; forms white fumes with hydrochloric acid, and unites with acids, producing rise of temperature. Altogether, it appears to be a stronger base than toluidine.—*Hydrochlorate of benzylamine*, $C^7H^9N.HCl$, crystallises in striated tables; the *chloroplatinate* in orange-coloured laminæ.

Dibenzylamine, $(C^7H^7)^2HN$, isomeric with benzyltoluidine, has not been isolated, but appears to be formed, together with mono- and tri-benzylamine, in the process above described.

Tribenzylamine, $(C^7H^7)^3N$, isomeric with dibenzyltoluidine (p. 866), has been already described (i. 574).

Phenyl-benzylamine, $C^{13}H^{13}N = \left.\begin{matrix}C^6H^5\\C^7H^7\\H\end{matrix}\right\}N.$ (Fleischer, Ann. Ch. Pharm. cxxxviii. p. 225; Bull. Soc. Chim. [1866], ii. 235.)—This base, isomeric with Hofmann's tolylaniline (iv. 454), is produced by mixing aniline with benzylic chloride (boiling at 170°).* The mixture becomes hot, and deposits white crystals, consisting of hydrochlorate of aniline, together with phenyl-benzylamine:

$$C^7H^7Cl + 2C^6H^7N = C^6H^7N.HCl + C^{13}H^{13}N.$$

The mixture must be heated to 160° for twenty-four hours, to complete the reaction; and on dissolving out the hydrochlorate of aniline from the product by water, the phenyl-benzylamine remains as an oil, which is converted by hydrochloric acid into crystals of the hydrochlorate, $C^{13}H^{13}N.HCl$. On decomposing this salt with soda, and distilling the liberated base under a pressure of 45 millimetres, the greater part passes over, between 200° and 220°, in the form of an oily liquid, which solidifies at a low temperature, and may be purified by pressure between bibulous paper, and recrystallisation from boiling alcohol.

Phenyl-benzylamine crystallises in colourless four-sided prisms, insoluble in water, but soluble in alcohol and in ether. It melts at 32°, remains in a state of surfusion at 12°, and boils under the ordinary pressure at a temperature above 310°. (Tolylaniline melts at 87°, and boils at 334°).—The *hydrochlorate*, $C^{13}H^{13}N.HCl$, forms colourless crystals.—The *oxalate*, $(C^{13}H^{13}N)^2.C^2H^2O^4$, forms white laminæ.—The base forms, with *chloride of cadmium*, the compound $C^{13}H^{13}N.CdCl^2$.

Phenyl-benzylamine, fused with mercuric chloride, forms at first a green mass, which dissolves in alcohol with fine blue colour; but by the prolonged action of heat, this mass assumes a dark colour, and then forms with alcohol a crimson solution.

Phenyl-benzylamine treated with *chloride of benzoyl* forms phenyl-benzyl-benzamide, $(C^6H^5)(C^7H^7)(C^7H^5O)N$, which crystallises in oblique prisms.

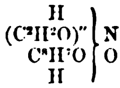
TOLUOL. Syn. with TOLUENE.

TOLUOLIC ACID. Syn. with TOLUIC ACID.

TOLUONITRILE. Syn. with BENZYLCYANIDE (i. 573).

TOLUOSALICYL, or **TOLUOSALICYLOL.** See SALICYLOL (p. 170).

TOLUOXYL. C^8H^7O.—The radicle of toluic acid and its derivatives. (Footnote, p. 869.)



TOLURIC ACID. $C^{10}H^{11}NO^3 = \left.\begin{matrix}H\\(C^2H^2O)''\\C^8H^7O\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$.—*Toluglycic Acid. Glycocol-toluic Acid.* (Kraut, Ann. Ch. Pharm. xcviii. 360.)—An acid homologous with

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* Chlorotoluene (according to Fleischer), but the boiling-point shows that the compound used was really benzylic chloride (p. 851).

hippuric acid, produced in the passage of toluic acid through the animal body, just as hippuric acid is formed from benzoic acid (iii. 158). To obtain it, toluic acid is swallowed in doses of several grammes (which may be done without injury to the health); the acid urine afterwards voided is evaporated to a syrup; this residue is exhausted with alcohol; the solution is mixed with oxalic acid and left to evaporate; and the residue is finally exhausted with alcoholic ether. The yellowish toluric acid still contaminated with oxalic acid, which remains on evaporating this last solution, is boiled with calcic carbonate; the calcium-salt, which crystallises out on cooling, is purified by repeated crystallisation, and then decomposed by heating it with dilute hydrochloric acid; and the acid, which crystallises out on cooling, is purified by solution in boiling water. It may be obtained in large crystals, by spontaneous evaporation of the alcoholic solution.

Toluric acid crystallises from boiling water in colourless laminæ; from alcohol in trimetric prisms, exhibiting the combination $\infty P \,.\, \infty\bar{P}\infty \,.\, \bar{P}\infty$, also with oP; they are as hard as gypsum, and have a vitreous and nacreous lustre. The acid is inodorous, melts at 160°—165°, and decomposes at a stronger heat, emitting an aromatic odour. It dissolves freely in boiling water, slightly in cold water; in almost any proportion of hot alcohol, abundantly also in cold alcohol, sparingly in ether free from alcohol.

Toluric acid, boiled with hydrochloric acid, is resolved, similarly to hippuric acid, into toluic acid and glycocine:

$$\underset{\text{Toluric acid.}}{C^{10}H^{11}NO^3} + H^2O = \underset{\text{Toluic acid.}}{C^8H^8O^2} + \underset{\text{Glycocine.}}{C^2H^5NO^2}.$$

Tolurates.—Most of these salts are soluble in water, those of the alkali-metals being the most soluble.

The *barium-salt*, $C^{20}H^{20}Ba''N^2O^6.5H^2O$, crystallises in small needles, apparently trimetric, exhibiting the faces ∞P, $\infty P\infty$; it dissolves easily in hot water.—The *calcium-salt*, $C^{20}H^{20}Ca''N^2O^6.3H^2O$, forms flattened crystals, one or two millimetres long, and strongly streaked parallel to their axis; very soft, and having a silky lustre; sparingly soluble in cold, easily in hot water.—The *silver-salt*, $C^{10}H^{10}AgNO^3$, obtained by double decomposition, is very soluble in hot water, and separates in well-defined crystals on cooling.—The *sodium-salt* crystallises from water in feathery needles.

The solution of the sodium-salt forms a white precipitate with neutral acetate of lead, brownish-yellow with ferric chloride. The latter precipitate is soluble in alcohol, and melts partially when boiled with water.

TOLUYL. C^8H^9.—The radicle of toluylic alcohol and its allied compounds;* isomeric with xylyl. Free toluyl, $\left.\begin{matrix}C^8H^9\\C^8H^9\end{matrix}\right\}$, obtained by the action of sodium on toluylic chloride, is a thick liquid, boiling at 296°. (**Vollrath**, Zeitschr. f. Chem. [2], ii. 488; Bull. Soc. Chim. [1867], i. 343.)

TOLUYLAMINE. A name sometimes applied to toluidine.

TOLUYLENE. A name sometimes given to tolylene or benzylene, C^7H^6, but more properly belonging to the hydrocarbon C^8H^8.

TOLUYLIC ACETATE, $C^2H^3(C^8H^9)O^2$, obtained by the action of toluylic chloride on acetate of potassium, or (better) on acetate of silver, is a liquid having an agreeable odour, and boiling at 226°. Alcoholic potash easily converts it into toluylic alcohol.

TOLUYLIC ACID. Syn. with TOLUIC ACID (p. 861).

TOLUYLIC ALCOHOL. $C^8H^{10}O = \left.\begin{matrix}C^8H^9\\H\end{matrix}\right\}O$. *Toluic* or *Toluenylic Alcohol.* (**Cannizzaro**, Compt. rend. liv. 1225; Jahresb. 1862, p. 267.)—An alcohol isomeric with xylylic alcohol, obtained: 1. By the action of alcoholic potash on toluic aldehyde (**Cannizzaro**):

$$\underset{\substack{\text{Toluylic}\\\text{aldehyde.}}}{2C^8H^8O} + KHO = \underset{\substack{\text{Toluate}\\\text{of potas-}\\\text{sium.}}}{C^8H^7KO^2} + \underset{\substack{\text{Toluylic}\\\text{alcohol.}}}{C^8H^{10}O}.$$

2. By the action of alcoholic potash on toluylic acetate (**Vollrath**). It is a white crystalline body, which melts at 58·5°—59·5°, and boils at 217° (xylylic alcohol is an oil, which merely becomes viscid at —18°, and boils at about 220°). Toluylic alcohol is slightly soluble in cold water, somewhat more freely in boiling water, and separates

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* The name toluyl is also applied, sometimes, to C^8H^7O, the radicle of toluic acid; sometimes to the radicle C^7H^7, more properly called **tolyl**; which latter name, on the other hand, is given by Vollrath to the radicle C^8H^9. To avoid all this confusion, it is advisable to designate C^7H^7 as **tolyl** or **benzyl**, C^8H^9 as **toluyl**, and C^8H^7O as **oxytoluyl** or **toluoxyl**.

therefrom in oily drops, which afterwards solidify in needle-shaped crystals; it is easily soluble in alcohol and in ether. Nitric acid converts it into toluic aldehyde. Heated in a stream of chlorine-gas, it is converted into toluylic chloride, C^8H^9Cl; and this compound, heated with cyanide of potassium in alcoholic solution, is transformed into toluylic cyanide, $C^9H^9N = C^8H^9CN$, which, when distilled with potash, yields alphatoluic acid (p. 864).

TOLUYLIC CHLORIDE, C^8H^9Cl (Vollrath, Zeitschr f. Chem. [2], ii. 488), produced by the action of chlorine on xylene, C^8H^{10}, at the boiling heat, is a liquid having a disagreeable odour, and boiling at 193°. When treated with cyanide of potassium, in presence of alcohol, and then with potash, it yields alphaxylylic acid, $C^9H^{10}O^2 = C^6H^4\left\{\begin{matrix}CH^3\\ CH^2.COHO.\end{matrix}\right.$ (See Xylylic Acid.)

TOLUYLIC SULPHIDE and **SULPHYDRATE.** Both sulphide and sulphydrate of potassium act very strongly on toluylic chloride, producing in the one case the sulphide of toluyl, $(C^8H^9)^2S$, in the other sulphydrate, $C^8H^9.H.S$. Both these compounds are liquids of disagreeable odour. The sulphydrate forms a bulky white precipitate with an alcoholic solution of mercuric chloride, and yellow with acetate of lead. (Vollrath.)

TOLYL, or **BENZYL.** $C^7H^7 = C^6H^4(CH^3)$.—A monatomic radicle, which may be supposed to exist in benzylic alcohol, benzylamine, tolylic or benzylic bromide, chloride, &c. The name *benzyl* is the most convenient for it, as tolyl is too much like toluyl.

Benzyl in the free state, $C^{14}H^{14}$, is obtained by heating benzylic chloride with excess of sodium to 100°, treating the product with ether, and evaporating the ethereal solution. It then remains as an oily body, which crystallises, after some time, in needles and laminæ. When purified by pressure between paper, and repeated crystallisation from strong alcohol, it forms white monoclinic crystals, exhibiting the combination $\infty P\infty \,.\, +P\infty \,.\, -P\infty \,.\, oP \,.\, -\tfrac{1}{3}P\infty$, tabular from predominance of $-P\infty$, and indistinctly cleavable parallel to ∞P and $[\infty P\infty]$. The following angular magnitudes have been approximately determined: $\infty P\infty : +P\infty = 150°$; $[\infty P\infty] : +P = 132°$; $oP : +P\infty = 131\tfrac{1}{2}°$. Benzyl melts between 51·5° and 52·5°, distils without decomposition at 284°, is insoluble in water, but dissolves in alcohol, ether, and sulphide of carbon. (Cannizzaro and Rossi, Ann. Ch. Pharm. cxxi. *250; Jahresb.* 1861, p. 548.)

Benzyl is likewise produced by the action of sodium on bromide of benzylidene, $C^7H^6Br^2$ (p. 853). Sodium acts rapidly on this compound at 180°, hydrobromic acid being given off, and a thick black mass formed, which is partly soluble in ether. On distilling the soluble portion of the product, toluene is given off at 109°; and the black resinous residue, if further distilled in a stream of aqueous vapour, gives off an oily liquid, which soon solidifies to a crystalline mass of benzyl, $C^{14}H^{14}$ (Michaelson and Lippmann, Ann. Ch. Pharm. Suppl. iv. 113; Jahresb. 1865, p. 550). The authors regarded the product thus obtained as isomeric with benzyl, and called it isobenzyl, because it appeared to unite directly with bromine, instead of forming substitution-products, like the benzyl obtained by the process of Cannizzaro and Rossi; but Fittig has shown (Ann. Ch. Pharm. cxxxvii. 271), that benzyl obtained by either process acts in the same manner with bromine.

Several substitution-derivatives of the molecule $C^{14}H^{14}$, called **dibenzyl-compounds**, have been obtained by Stelling and Fittig (Ann. Ch. Pharm. cxxxvii. 257; Jahresb. 1865, p. 547).

Amidobenzyl, or *Diamidodibenzyl*, $C^{14}H^{16}N^2 = C^{14}H^{12}(NH^2)^2$, is produced by reducing nitrobenzyl (p. 871) with tin and strong hydrochloric acid, and is thrown down by ammonia—from the solution previously freed from tin—as an amorphous precipitate. It resembles the homologous compound, amidophenyl or benzidine (iv. 411), and crystallises from hot water in colourless scales, which are nearly insoluble in cold water, very soluble in alcohol, melt at 132°, and sublime, almost without decomposition, at a higher temperature. It is a base, and forms crystalline salts.

The *hydrochlorate*, $C^{14}H^{16}N^2.2HCl$, is very soluble in water and alcohol, and separates from strong hydrochloric acid in small colourless crystals.—The *chloroplatinate*, $C^{14}H^{16}N^2.2HCl.PtCl^4$, forms easily decomposable needles, united in concentric groups. —The *sulphate*, $C^{14}H^{16}N^2.H^2SO^4$, is a white crystalline powder, slightly soluble in water.—The *neutral oxalate*, $C^{14}H^{16}N^2.C^2H^2O^4$, is a crystalline precipitate; the *acid oxalate*, $C^{14}H^{16}N^2.2C^2H^2O^4.3H^2O$, is deposited in hard, transparent, prismatic crystals, nearly insoluble in cold water.—The *phosphate* is a white precipitate.—The *chromate* forms easily decomposable yellow needles.

Isonitrobenzyl is easily reduced by tin and hydrochloric acid to a base, which soon changes to a tarry mass.

Bromobenzyls.—Benzyl, suspended in water and mixed with bromine, yields a pasty mass consisting of several substitution-products. On dissolving the product, decolorised with soda-ley, in hot alcohol, dibromodibenzyl crystallises out first, while the monobrominated compound remains in solution.—*Monobromodibenzyl*, $C^{14}H^{13}Br$, when purified by distillation, is a colourless viscid oil, having a specific gravity of 1·398 at 9°. It solidifies below 0°, in the crystalline form, boils at a temperature above 310°, and, like the following compound, is not decomposed by heating to 140° with alcoholic solution of ammonia, iodide of potassium, or cyanide of potassium.—*Dibromodibenzyl*, $C^{14}H^{12}Br^2$, is nearly insoluble in cold alcohol and benzene, very sparingly soluble in hot alcohol, melts at 114°—115°, and crystallises in colourless prisms or needles.—*Tribromodibenzyl*, $C^{14}H^{11}Br^3$ (or, perhaps, $C^{14}H^{12}Br.Br^2$), is formed, together with dibromodibenzyl, when the quantity of bromine used is sufficient to cause the mass, which is pasty at first, to become solid and friable. It is still less soluble in alcohol than the dibrominated compound, and in the pure state forms nacreous laminæ, which decompose at 170°, without previous fusion.—*Hexbromodibenzyl*, $C^{14}H^8Br^6$, is obtained by bringing dibromodibenzyl in contact with excess of bromine, and recrystallising the product from benzene, in hard, colourless, well-defined prisms, nearly insoluble in alcohol.

Bromide of Benzyl, or *Dibromide of Dibenzyl*, $C^{14}H^{14}Br^2$.—This compound is formed, together with monobromobenzyl, by adding bromine to an ethereal solution of benzyl; and crystallises in colourless silky needles, not fusible without decomposition. It dissolves in boiling alcoholic potash, with formation of monobromodibenzyl. (Michaelson and Lippmann; Fittig.)

Nitrobenzyl, or *Dinitrodibenzyl*, $C^{14}H^{12}(NO^2)^2$.—Fuming nitric acid acts violently on benzyl, even in the cold, converting it into two isomeric nitro-compounds, which may be separated from one another by crystallisation from alcohol. The hot saturated solution first deposits long slender needles of nitrobenzyl, insoluble in water, only slightly soluble in hot alcohol, ether, chloroform, or benzene, and melting at 106°—107°. The mother-liquor, when concentrated, deposits the more soluble *isonitrobenzyl*, partly in crystalline nodules, partly as a thick oil. This compound crystallises from alcohol in extremely fine needles, which form a bulky woolly mass when dry, and melt at 74°—75°. These nitro-compounds are reduced, by tin and hydrochloric acid, to the corresponding amido-compounds (p. 870).

Nitrobromobenzyl, $C^{14}H^{10}(NO^2)^2Br^2$, is produced by dissolving bromobenzyl in warm fuming nitric acid. When purified by washing the crystals which separate on cooling, with hot alcohol, and recrystallising the undissolved powder from benzene, it forms well-developed sword-shaped crystals, which melt at 204°—205°, are nearly insoluble in hot alcohol, more soluble in hot benzene.

TOLYLACETAMIDE, or **BENZYLACETAMIDE**, $C^9H^{11}NO^2 = \left.\begin{matrix}C^7H^7\\C^2H^3O\\H\end{matrix}\right\}N$, or **ACETOTOLUIDE**, $C^7H^6(C^2H^3O).NH^2$. (Riche and Bérard, Ann. Ch. Pharm. cxxix. 77; Jahresb. 1863, p. 428.—Städeler and Arndt, Jahresb. 1864, p. 426.)—This compound, homologous with phenylacetamide (iv. 418), is produced by distilling 1 at. toluidine with 1 at. acetic acid, and remains, on treating the last portion of the distillate with acidulated water, as a white residue melting at 145° (Riche and Bérard). It is likewise formed in the manufacture of aniline by reduction of commercial nitrobenzene with iron and acetic acid. The viscid oils which pass over towards the end of the operation, contain a solid body which, when purified by pressure between paper and repeated crystallisation, exhibits the composition of acetoluide (Riche and Bérard). Städeler and Arndt found the solid mass, obtained by repeated distillation of crude commercial aniline with glacial acetic acid, to consist chiefly of acetanilide and acetoluide. The latter was separated by solution in strong sulphuric or acetic acid, precipitation with water, and crystallisation, or sublimation in a stream of carbonic anhydride.

Acetoluide, when sublimed or quickly crystallised, forms small slender needles like sublimed benzoic acid; by slow crystallisation, it is obtained in longer and thicker brittle needles. It is tasteless, and at ordinary temperatures inodorous, melts at 145°—145·5°, evolving aromatic cough-exciting vapours, and boils at 310°—350°. It is sparingly soluble in cold water (in 1786 pts. 6·5°), easily soluble in boiling water, also in alcohol and ether. It dissolves in concentrated acids, and is precipitated therefrom by water—not decomposed by boiling with dilute acids, or with aqueous alkalis (Städeler and Arndt). According to Riche and Bérard, it is slowly decomposed by boiling with aqueous potash, and quickly by distillation over fused potassium-hydrate, into toluidine and acetic acid; the same decomposition is easily produced by alcoholic potash (Städeler and Arndt). Its solution in strong sulphuric acid acquires a fine green colour on addition of potassic chromate. (Städeler and Arndt.)

TOLYLAMINE. Syn. with Benzylamine (p. 867).

TOLYLANILINE. $C^6H^4(C^7H^7).NH^2$.—A base isomeric, if not identical, with phenyltoluidine (iv. 454; v. 866).

TOLYLBENZAMIDE, BENZYLBENZAMIDE, or **BENZOTOLUIDE,** $C^{14}H^{13}N = C^7H^7.C^7H^5O.HN = C^7H^6(C^7H^5O).NH^2$. (Jaillard, Compt. rend. lx. 1096; Jahresb. 1865, p. 428.)—Prepared by treating chloride of benzoyl with toluidine, washing the resulting hard mass with acidulated water, and dissolving it in boiling alcohol of 90 per cent. It then crystallises, on cooling, in long, colourless, and inodorous needles, insoluble in water, easily soluble in alcohol and in ether. It melts at 100°, and volatilises without decomposition at 232°. When heated with alkalis, it is resolved into benzoic acid and toluidine.

TOLYLCARBAMIDE, BENZYLCARBAMIDE, or **CARBOTOLUIDE.** $C^8H^{10}N^2O = \left.\begin{matrix}(CO)''\\ C^7H^7\\ H^3\end{matrix}\right\}N^2$.—*Benzyl-urea* (Sell, Chem. Soc. J. xvi. 190; Jahresb. 1865, p. 426) separates, on mixing a hot aqueous solution of toluidine-sulphate with a recently prepared solution of potassium-cyanate, in white needles, which have a sweetish taste, dissolve sparingly in cold, easily in hot water, also in alcohol and in ether, and are resolved, at 158°, into ammonia and ditolylcarbamide. It is related to the isomeric compound obtained by Noad from nitrotolylamide, in the same manner as the true phenyl-urea to the compound which Chancel obtained by reduction of nitrobenzamide (See Carbamides, i. 754, 755.)

Tolyl-ethylcarbamide, $C^{10}H^{14}N^2O = (CO)''(C^7H^7)(C^2H^5)H^2N^2$, is obtained by direct combination of toluidine with ethylic cyanate, and separates from a boiling mixture of alcohol and water, in white crystals. It is insoluble in water, but soluble in alcohol. (Sell, *loc. cit.*)

Ditolylcarbamide, $C^{15}H^{16}N^2O = (CO)''(C^7H^7)^2H^2N^2$, is produced by boiling an alcoholic solution of ditolylsulphocarbamide with mercuric oxide, as long as mercuric sulphide is thereby separated. The filtered solution yields ditolylcarbamide in white crystals. It is likewise obtained, together with the products of decomposition of ordinary urea, by the dry distillation of monotolylcarbamide. It is insoluble in water, easily soluble in alcohol, and is decomposed by strong sulphuric acid, in the manner shown by the equation, into tolylsulphamic or sulphotolylamic acid, carbonic anhydride, and water (p. 527):

$$C^{15}H^{16}N^2O + 2H^2SO^4 = 2(C^7H^9N.SO^3) + CO^2 + H^2O.$$

Ditolylsulphocarbamide, $C^{15}H^{16}N^2S = \left.\begin{matrix}(CS)''\\ (C^7H^7)^2\\ H^2\end{matrix}\right\}N^2$, is obtained by warming a concentrated alcoholic solution of toluidine with an equal volume of carbonic disulphide, not above 80°, till the evolution of sulphydric acid ceases, distilling off the excess of carbonic disulphide, and recrystallising the remaining crystalline mass from alcohol. It is insoluble in water and in cold alcohol, has a bitter taste, and forms large acuminated prisms, which melt at 164°, and sublime without decomposition. (Sell.)

TOLYL-DIPHENYL-ROSANILINE. See Phenylamines (iv. 473).

TOLYLENE. C^7H^6.—Syn. with Benzylene (i. 577).

TOLYLENE-DIAMINE. $C^7H^{10}N^2 = \left.\begin{matrix}(C^7H^6)''\\ H^4\end{matrix}\right\}N^2$. (Hofmann, Proc. Roy. Soc. xi. 518.)—This base, first obtained as a by-product in Colin's aniline factory at Paris, is prepared by distilling dinitrotoluene with a mixture of iron-filings and acetic acid. When recently prepared, it forms crystals which become slightly coloured on exposure to the air, but may be rendered colourless again by treatment with animal charcoal. It melts at 99°, and distils without decomposition at about 280°. It is dissolved in considerable quantity by boiling water, and separates on cooling in needles, sometimes an inch long. It is easily soluble in alcohol and ether. Its solutions have an alkaline reaction.

Hydrobromate of tolylene-diamine, $C^7H^{10}N^2.2HBr$, forms short needle-shaped crystals, soluble in water and in alcohol.—The *hydrochlorate* is easily soluble in water, even at ordinary temperatures, but crystallises easily from strong hydrochloric acid.—The *chloroplatinate* forms yellow needles, very easily soluble in water.—The *sulphate*, $C^7H^{10}N^2.H^2SO^4$, forms long well-defined needles, which become reddish on exposure to the air.

Tolylene-diamine, treated with œnanthol, forms diœnanthylidene-tolylene-diamine, $C^{21}H^{24}N^2 = (C^7H^{14})^2(C^7H^6)''N^2$, as a heavy non-basic oil, soluble in alcohol, but insoluble in water. With bitter-almond-oil, in like manner, it yields dibenzylidene-tolylene-diamine, $C^{21}H^{18}N^2 = (\alpha C^7H^6)''(\beta C^7H^6)''N^2$. (Schmidt, Jahresb. 1865, p. 429.)

TOLYLENE-TRIAMINES. (De Laire, Girard, and Chapoteaut, Compt. rend. lxiii. 964; liv. 416.)—Hofmann has shown that rosaniline (iv. 468) has the composition of ditolylene-phenylene-triamine, $(C^7H^6)^2(C^6H^4)H^3N^3$, being formed by elimination of 6 at. hydrogen from a mixture of 2 at. toluidine and 1 at. aniline. Other bases of similar constitution may be obtained by the action of oxidising or dehydrogenising agents on toluidine, aniline, and mixtures of the two:

a. Tritolylene-triamine, or *Chrysotoluidine*, $C^{21}H^{21}N^3 = \left.\begin{matrix}(C^7H^6)^3\\ H^3\end{matrix}\right\}N^3$, is a yellow base, resulting from the oxidation of 3 at. toluidine:

$$3(C^7H^7)H^2N - H^6 = (C^7H^6)^3H^3N^3.$$

β. Triphenylene-triamine, or *Violaniline*, $C^{18}H^{15}N^3 = \left.\begin{matrix}(C^6H^4)^3\\ H^3\end{matrix}\right\}N^3$, is a violet base, formed, in like manner, from 3 at. aniline.

γ. Diphenylene-tolylene-rosaniline, or *Mauvaniline*, $C^{19}H^{17}N^3 = \left.\begin{matrix}(C^6H^4)^2\\ (C^7H^6)''\\ H^3\end{matrix}\right\}N^3$.—This base is formed (together with violaniline and a small quantity of rosaniline) when the aniline used is not quite free from toluidine:

$$\underset{\text{Aniline.}}{2(C^6H^5)H^2N} + \underset{\text{Toluidine.}}{(C^7H^7)H^2N} - 3H^4 = \underset{\text{Mauvaniline.}}{(C^6H^4)^2(C^7H^6)H^3N^3}.$$

Mauvaniline is a crystallised base of light-brown colour, becoming darker when heated. The crystals are hydrated, containing $2C^{19}H^{17}N^3.H^2O$. They retain their water at 120°—130°, and give it up only at a temperature at which they begin to decompose.

Mauvaniline is soluble in alcohol, ether, and benzene, insoluble in cold, very soluble in boiling water. It dissolves in acids, forming crystallisable salts, which have a bronze-green reflex, like those of rosaniline. They are slightly soluble in cold, moderately soluble in boiling water, and in strongly acidulated water. They rival the salts of rosaniline in tinctorial power, imparting a fine mauve colour to silk and wool.

Violaniline, mauvaniline, rosaniline, and chrysotoluidine, form an arithmetic series, whose common difference is CH^2. The formation of violaniline, mauvaniline, and chrysotoluidine being strictly analogous to that of rosaniline, these bodies may also be expected to result from the oxidation of commercial aniline. It is well known, indeed, that the quantity of rosaniline obtained in the preparation on the large scale is considerably less than that which corresponds to the quantity of aniline and toluidine transformed, and that there is produced, at the same time, a quantity of resinous matter, of violet to brownish-yellow colour, and possessed of basic properties. This resinous matter is a mixture of several compounds, extremely difficult to separate, and doubtless consisting in great part of the three homologues of rosaniline just mentioned. The authors have, in fact, detected mauvaniline in the residues of the preparation of rosaniline-salts; they likewise attribute the decided violet tint exhibited by certain commercial aniline-reds to the presence of mauvaniline, and the yellow tint sometimes observed in commercial rosaniline-salts to admixture of chrysotoluidine.

δ. The three atoms of typic hydrogen in each of the bases above mentioned may be replaced by alcohol-radicles, ethyl, methyl, phenyl, tolyl, &c., forming derivatives analogous to triethyl- and triphenyl-rosaniline (iv. 471, 472), and obtainable by similar methods.

ε. The secondary monamines, diphenylamine, ditolylamine, methyl-phenylamine, &c., subjected to the action of dehydrogenising agents, likewise give off 6 at. hydrogen, and yield substituted triamines of rosaniline, chrysotoluidine, and violaniline; *e.g.*:

$$\underset{\text{Ditolylamine.}}{3(C^7H^7)H^2N} - H^6 = \underset{\text{Tritolyl-chryso-toluidine.}}{\left.\begin{matrix}(C^7H^6)^3\\ (C^7H^7)^3\end{matrix}\right\}N^3}.$$

TOLYL-ETHYL-UREA. Syn. with TOLYL-ETHYL-CARBAMIDE (p. 872).

TOLYL-PHENYLAMINE. Syn. with TOLYLANILINE (iv. 454).

TOLYLSALICYLAMIDE. This name is given by Jaillard (Compt. rend. lx. 1096) to a compound obtained by heating a mixture of toluidine and salicylol to 50°, and crystallising the product from hot alcohol. It forms yellow crystals, inodorous, insoluble in water, soluble in alcohol and ether, melts at 100°, volatilises at a higher temperature, and is decomposed by alkalies. According to **Jaillard**, it has the same composition as tolylbenzamide, $C^{14}H^{13}NO$, and its hydrochlorate gives, with platinic chloride, a double salt, containing $2(C^{14}H^{13}NO.HCl)Pt.Cl^4$.

TOLYLSUCCINIMIDE, or **SUCCINOTOLUIDE.** $C^{11}H^{11}NO^2 = \left.\begin{matrix}(C^4H^4O^2)''\\ C^7H^7\end{matrix}\right\}N = C^7H^5(C^4H^4O^2)''.NH^2$.—This compound is formed by melting equal weights of succinic acid and toluidine, and crystallising the cooled mass from boiling water. It volatilises without decomposition, dissolves easily in hot water, alcohol, and ether, and separates from solution in colourless crystals.

Ditolylsuccinamide, $C^{18}H^{20}N^2O^2 = \left.\begin{matrix}(C^7H^7)^2\\ (C^4H^4O^2)''\\ H^2\end{matrix}\right\}N^2$, is the portion of the above-mentioned product insoluble in hot water; it crystallises from hot alcohol. (**Sell.**)

TOLYLSULPHUROUS BROMIDE and **CHLORIDE.** Syn. with TOLUENE-SULPHOBROMIDE and TOLUENE-SULPHOCHLORIDE (p. 859).

TOLYLSULPHUROUS HYDRIDE. Syn. with TOLUENE-SULPHUROUS ACID (p. 860).

TOLYL-THIOSINAMINE. By heating toluidine with oil of mustard to 100° for several hours, a mass is formed, which solidifies in laminæ on cooling, and may be purified by recrystallisation from alcohol. It is inodorous, insoluble in water, easily soluble in alcohol and ether, melts at 100°, and is converted, by oxide of lead or mercury, into a non-sulphuretted compound, which crystallises in needles. (**Jaillard.**)

TOMBAC. An alloy of copper and zinc containing about 80 per cent. copper. (See COPPER, ALLOYS OF, ii. 47, 49.)

TOMBAZITE. Breithaupt's name for a variety of nickel-glance from a mine near Lobenstein.

TONKA-BEANS. The fruit of *Dipterix odorata* a leguminous tree, indigenous in Guiana. They are about the size of a large almond, rather cylindrical than flat, and pointed at both ends. The outer shell is dark-brown, wrinkled, and has a fatty lustre. The beans have an aromatic bitter taste, and a very agreeable odour, like that of melilot and woodruff. They contain coumarin (ii. 93), and a fixed oil, besides sugar, gum, starch, malic acid, salts, and woody fibre (**Boullay** and **Boutron-Charlard**, J. Pharm. xi. 426; *ibid.* [3] vii. 160). They are used as a perfume, especially for snuff.

The so-called English tonka-beans (from *Dipterix oppositifolia*) are rather smaller and darker, but otherwise not essentially different from those just described.

TOPAZ. *Physalite. Pyrophysalite. Pycnite. Schorlartiger Beryl. Stangenstein.*—A tribasic silicate of aluminium, $Al^2O^3.SiO^2$, having part of the oxygen replaced by fluorine. It occurs in trimetric crystals, exhibiting the combination $P . \infty P$, $\infty\breve{P}2$, like *fig.* 265 (ii. 147), also with the basal face oP, and the face $2\breve{P}\infty$ replacing the terminal edges between P and P; frequently also with other faces subordinate. Axes $a : b : c = 0{\cdot}5285 : 1 : 0{\cdot}4770$. Angle $P : P$ (brach.) = 141° 0′; $P : P$ (macr.) = 101° 40′; $P : P$ (basal) = 87° 18′. The crystals are usually hemimorphous, the extremities being unlike. Cleavage very perfect parallel to the base. The mineral also occurs granular, coarse or fine. Hardness = 8. Specific gravity = 3·4—3·65. Lustre vitreous. Colour yellow, white, green or blue; pale. Streak uncoloured. Transparent to subtranslucent. Fracture subconchoïdal to uneven. Pyroelectric. Before the blowpipe on charcoal, it does not fuse, but when strongly heated becomes covered with small blisters, which crack as soon as formed. The pale-yellow varieties become colourless when heated, the dark-yellow become rose-red or hyacinth-red. When strongly heated in a glass tube with microcosmic salt, it exhibits the fluorine reaction. With borax it slowly fuses before the blowpipe to a colourless glass; with microcosmic salt it forms a silicious skeleton, the bead becoming opalescent on cooling; with carbonate of sodium it forms a tumid, semitransparent slag; with a large quantity of the sodium-salt, a tumefied infusible mass. It is insoluble in acids; and when digested for some time with strong sulphuric acid, it gives off hydrofluoric acid.

The analyses of topaz from Fahlun in Sweden, and Trumbull in Connecticut, by **Forchhammer** (J. pr. Chem. xxix. 294; xxx. 400), give from 34·39 to 35·66 per cent. silica, 51·88 to 55·96 alumina, and about 17 per cent. fluorine, showing that topaz may be regarded as a mixture or compound of tribasic aluminium-silicate with silico-aluminic fluoride in the proportion represented by the formula $(2Al^2F^3.SiF^4).5(Al^2O^3.SiO^2)$. The older analyses by Berzelius, Vauquelin, and Klaproth gave the amount of fluorine about 3 per cent. too low.

Topaz occurs in gneiss or granite, with tourmaline, mica, and beryl, occasionally with apatite, fluor-spar, and tin; also in talcose rock, as in Brazil, with euclase, &c., or in mica-slate. Fine topazes come from the Ural and Altai Mountains, from Miask in Siberia, and from Kamtschatka, of green and blue colours; from Villa Rica in Brazil, of deep yellow colour: blue crystals occur at Cairngorm, Aberdeenshire, and in the tin-mines of Schlackenwald, Zinnwald, and Ehrenfriedersdorf; smaller crystals also at Schneckenstein and Altenberg in Saxony, and on the Mourne Mountains in Ireland.—*Pycnite* is a massive, subcolumnar variety of topaz from Altenberg, Schlackenwald, Zinnwald, and Kongsberg.—*Physalite*, or *Pyrophysalite*, is a coarse nearly opaque variety, which intumesces when heated. It is found in yellowish-white crystals, of considerable size, at Fossum in Norway, and at Finbo and Broddbo in Finland; a crystal was found in this last locality, weighing eighty pounds. Topaz occurs in the United States, at Trumbull and Middletown in Connecticut, and at Crowder's Mountain, North Carolina.

The finer varieties of topaz are much valued as gems. The best crystals are brought from Minas Geraes in Brazil. The coarse varieties may be employed as a substitute for emery.

TOPAZ ROCK. This name was applied by Werner to a rock composed of quartz, tourmaline, lithomarge, and topaz, forming a considerable vein in the mica-slate of the Saxon Voigtland.

TOPAZOLITE. A name sometimes applied to yellow garnet.

TORBANITE, or **TORBANE HILL MINERAL.** See Coal (i. 1033).

TORBERITE. See Uranite.

TORMENTILLA. The roots of *Tormentilla erecta* were formerly used in medicine as *Red tormentilla*. They contain, in the fresh state, from 5 to 6 per cent. of a tannin, which, according to Stenhouse, forms a dark-green precipitate with ferrous sulphate, bluish-red with ferric acetate; it is also precipitated by gelatin and by tartar-emetic. It has been proposed to substitute this root for that of rhatany for use in medicine.

The leaves of the plant contain, according to Sprengel, 63 per cent. water, 33 dry vegetable substance, and 4 ash. The ash contains, in 100 pts., 12·0 per cent. potash, 3·0 soda, 22·7 lime, 2·3 magnesia, 10·3 ferric oxide, 5·1 alumina, 41·4 silica, 2·0 sulphuric anhydride, 0·5 phosphoric anhydride, and 0·8 chlorine.

TORPEDO. The electric organ of the *Torpedo Galvanii* has been examined by Schulze (Jahresb. 1859, p. 622). The aqueous extract contains a proportionally large quantity of urea and calcic phosphate, together with creatinine, syntonin, an organic body precipitable by tannin, and several compounds precipitable by chloride of zinc—some in the crystalline, others in the syrupy form. Respecting the electric properties of the torpedo, see Electricity (ii. 476).

The name *torpedo* is likewise applied to explosive engines, which are sunk in the water of harbours, and fired by electricity on the approach of a hostile vessel.

TORRELITE. Syn. with Niobite.

TORRICELLIAN VACUUM. The space above the mercury in a barometer-tube, which is free from air, but contains vapour of mercury; the tension of this vapour, however, is imperceptible at ordinary temperatures.

TOULOUCOUNA or **TULUCUNA OIL.** Syn. with Carapa Oil (i. 749).

TOULOURON OIL. A brown train-oil obtained from *Pagurus Latro*, and used by the negroes of Senegal as a remedy for rheumatism.

TOURMALINE. *Schorl. Rubellite. Indicolite. Aphrisite. Aphrite. Zeuxite.*—A well-marked group of rhombohedral double silicates, characterised geometrically and physically by hemimorphism and pyroelectricity, and chemically by the presence of boracic acid. The crystals usually exhibit the combination $\infty P2 . \frac{\infty R}{2}$, terminated by R and other rhombohedrons. The primary form may be assumed to be a rhombohedron R, having the principal axis equal to 0·4472, and the angle R : R in the terminal edges = 133° 10′; but the magnitude of the angle differs to a certain extent in the several varieties. The crystals exhibit traces of cleavage parallel to R. They are brittle, with subconchoïdal to uneven fracture.

Hardness = 7 to 7·5. Specific gravity = 2·94 to 3·3. Lustre vitreous. Colour black, brown, blue, green, red, or white; some specimens are red internally, and green externally; others red at one extremity, and green, blue, or black at the other. The crystals exhibit dichroism (iii. 670). Their streak is uncoloured. They are transparent to opaque; unlike in transparency across the prism, and in the line of the axis. Transparent tourmalines transmit light only when polarised in a plane perpendicular to their principal axis (iii. 655). The crystals are strongly pyro-electric (ii. 411).

The numerous analyses which have been made of tourmalines (for which see Rammelsberg's *Mineralchemie*, pp. 673–679; Dana's *Mineralogy*, ii. 272), show that these minerals contain, as protoxides, magnesia, ferrous oxide, manganous oxide, lime, lithia, potash, soda, and that the relative proportions of these bases, especially of the magnesia, ferrous and manganous oxides, vary within very wide limits: hence Rammelsberg, to whom the greater number of these analyses are due, divides tourmalines into magnesium-tourmalines, magnesium-iron tourmalines, iron-tourmalines, iron-manganese tourmalines, and manganese-tourmalines; the last two varieties contain lithia, the others do not. The sesquioxides contained in tourmalines are alumina, and, according to most authorities, likewise ferric and manganic oxides; according to A. Mitscherlich, however (J. pr. Chem. lxxxvi. 1), the iron and manganese in tourmalines are wholly in the state of protoxide. All tourmalines likewise contain boric oxide or anhydride, B^2O^3, which may be regarded as replacing part of the alumina. As the most general expression of the composition of tourmalines, Rammelsberg gives the formula:

$$(2\mathrm{M}^2\mathrm{O}.\mathrm{SiO}^2)\ .\ n(\mathrm{R}^2\mathrm{O}^3;\mathrm{B}^2\mathrm{O}^3)\mathrm{SiO}^2,$$

M denoting a monatomic metal (2 at. of which may of course be replaced by M''), and R a triatomic metal. Most tourmalines contain also a small quantity of fluorine, which (as in topaz) may be regarded as replacing part of the oxygen. For the full discussion of the formula, see Rammelsberg (*loc. cit.*).

The following are examples of the composition of the several varieties of tourmaline above enumerated, according to analyses by Rammelsberg:—

a. Magnesium-tourmaline, from Gouverneur, St. Lawrence County, New York: brown; specific gravity = 3·049.—*b.* Magnesium-iron tourmaline, from Texas, Lancaster County, Pennsylvania: very thin, dark-green, translucent; specific gravity = 3·043.—*c.* Iron-tourmaline, from Sonnenberg, near Andreasberg, in the Harz: specific gravity = 3·243 (the heaviest tourmaline).—*d.* Iron-manganese tourmaline, from Elba: green, often reddish or blackish at one end; specific gravity = 3·112.—*e.* Manganese-tourmaline, from Paris, in the State of Maine: dark-red; specific gravity = 3·019:

	a.	*b.*	*c.*	*d.*	*e.*
Fluorine . .	2·28	2·36	1·64	2·35	2·58
Phosphoric anhydride . .		0·20	0·12	. .	0·27
Silica . .	38·85	38·45	36·51	38·19	38·33
Boric anhydride	8·25	8·48	7·62	7·39	9·00
Alumina . .	31·32	34·56	32·92	39·16	43·15
Manganic oxide	. .	. .	. .	4·74	1·12
Ferric oxide .	1·27	3·31	8·13	3·14	
Ferrous oxide .	. .	0·09*	9·62†	?	
Magnesia . .	14·89	9 11	0·78	1·00	1·02
Lime . .	1·60	0·71	0·72	0·84	
Soda . .	1·28	2·00	1·36	2·40	2·60
Lithia . .	. .	. .	. .	0·74	1·17
Potash . .	0·26	0·73	0·58	0·34	0·68
Loss by ignition	3·19	3·30	2·31	3·28	3·61

The colour of tourmalines varies according to their composition: red tourmalines (*rubellite*, *siberite*, *daourite*, *apyrite*) are those which contain lithium and manganese, with little or no iron (manganese-tourmalines); the violet-blue and green varieties generally contain lithium, iron, and manganese (iron-manganese tourmalines); the black (*schorl*) are either iron- or magnesium-iron tourmalines; the yellow and brown mostly magnesium-tourmalines. Hence the chemical characters of tourmalines vary to a considerable extent, according to their colour.

Tourmalines not containing lithia, when heated before the blowpipe, form, with strong intumescence, and more easily in proportion as they contain more iron, white or yellowish masses, which afterwards melt to white, yellowish, or grey slags. Heated with fluor-spar and acid sulphate of potassium, they give—like all other tourmalines—the reaction of boric acid. Magnesium-iron tourmalines yield, after swelling up, a white, grey, yellowish, greenish, or brown slag; iron-tourmalines, after intumescence, brown or black slags; iron-manganese tourmalines (the dark-coloured or blue) melt before the blowpipe, with difficulty and slight intumescence, to grey or brownish slags, and, when heated in a furnace, bake together to compact dark-brown masses. Green tourmalines, heated before the blowpipe, become white and opaque, melt on very thin edges to an enamel covered with small bubbles, and when heated in a crucible, form porcelain-like masses without fusing; only the green tourmaline of Brazil, and that of Chesterfield in Massachusetts, swell up before the blowpipe, and yield, partly a greyish-yellow slag, partly an unfused violet-green mass; when strongly heated in a crucible, they form an opaque brownish slag. Manganese-tourmalines generally exfoliate before the blowpipe, becoming white and opaque, and, when heated in a crucible, sometimes sinter slightly together.

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* Manganous oxide. † Containing 0·11 manganous oxide.

At a strong red heat, all tourmalines lose several per cent. of their weight, in consequence of the escape of silicic fluoride, and perhaps also of boric fluoride. It is only after having undergone this change that the pulverised tourmaline can be decomposed by hydrofluoric acid; whereas this acid acts but slightly on the original tourmaline, and other acids still less or not at all. According to v. Kobell, pulverised tourmaline is imperfectly decomposed by sulphuric acid before fusion, almost completely after fusion.

Tourmalines are usually found in granite, gneiss, or mica-slate; they also occur in dolomite or granular limestone, and in sandstone near dykes of igneous rocks. Large black tourmalines occur in Greenland; at Hörlberg, near Bodenmais, in Bavaria; at Käringbricka, in Sweden, and near Bovey in Devonshire. Small brilliant crystals, occurring in decomposed felspar, at Andreasberg in the Harz, constitute the variety called *aphrite*. Rubellite and green tourmalines occur near Ekatherinenburg in Siberia; pink crystals are found in Elba; pale yellowish-brown crystals in talc at Windsch-Kappell in Carinthia; green at Airolo, in Switzerland; white specimens (*achroïte*) come from St. Gothard, Siberia, and Elba. Black tourmalines occur with the emery of Naxos. Magnificent red and green tourmalines have been found at Paris, in the State of Maine, some above an inch in diameter, transparent ruby-red within, surrounded by green or red at one extremity, and green at the other. (Respecting other American localities, see Dana, ii. 274.)

TOURMALINE, ARTIFICIAL. This name has been applied to sulphate of iodoquinine, on account of its optical properties. (See QUININE, p. 25.)

TOURMALINE-ROCK. TOURMALINE-SLATE. Tourmaline and quartz are found united in rocks like mica and quartz, and thus form tourmaline-rock and tourmaline-slate. The former is a crystallo-granular mixture, containing also crystals of felspar; in the latter, tourmaline, varying in structure from acicular to granular, occurs in alternate layers with granular quartz. These slates, by taking up mica, pass into mica-slate, or by taking up felspar into gneiss; the mixture called tourmaline-rock passes, in like manner, into tourmaline-granite. (Handw. d. Chem. viii. 1046.)

TOWANITE. Syn. with COPPER-PYRITES (ii. 77).

TRACHYDOLERITE. This name is applied to certain rocks, resembling both trachyte and dolerite in external appearance, and consisting of oligoclase or labradorite and amphibole or augite, with more or less magnetic iron-ore. The mixture is fine-grained, and usually forms a grey or brown mass, in which small crystals of the above-named minerals are imbedded. Specific gravity = 2·7 to 2·8. The proportion of silica in the rock is from 50 to 60 per cent. On the trachydolerite of the Siebengebirge, see Deiters (Inaugural dissertation; *De connexu inter trachyten et basalten, &c.*, Bonnæ. 1861; Jahresb. 1861, p. 1069); on that of Madeira and Porto Santo, Cochius (J. pr. Chem. xciii. 129; Jahresb. 1864, p. 872).

TRACHYTE. A felspathic rock, having a rough surface of fracture, and usually consisting of a fine-grained or compact ground mass of sanidin, oligoclase, albite, or labradorite, or two of these minerals together, enclosing crystals or crystalline particles of these felspars, also of amphibole or augite, and dark-coloured mica. When the felspathic ground-mass is decomposed, the rock becomes an indurated clay, and is then sometimes called domite; such an altered trachyte occurs on the Puy-de-Dôme. Nodules of trachyte, bound together by a trachytic cement, form trachyte-conglomerate or trachyte-breccia. Trachyte-porphyries are trachytes in which the ground-mass is more or less compact, and the imbedded crystals of sanidin are more distinct than in ordinary trachyte; the rock also frequently contains brown or black crystals of mica, and sometimes small crystals or grains of quartz. On the trachytes of the Eugenesian Mountains, near Padua, see G. v. Rath (Jahresb. 1865, p. 916); on those of Auvergne, Kossmann (*ibid.* 918).

TRAGACANTH. See GUM (ii. 955).

TRAGOPOGON. The goat's-beard, *Tragopogon pratensis*, a composite plant of tribenzylamine remains undissolved, and the solution contains, together with sal-ammoniac, the hydrochlorate of benzylamine, and probably also of dibenzylamine. The hydrochlorate of benzylamine is separated from the more soluble portion by fractional crystallisation; and the free base separated from this salt by potash is dissolved in ether, freed from ether by evaporation, dehydrated by fused potash out of contact with the air, and then distilled—the portion which gives over at 182° being collected apart. For complete purification, it is converted into the solid carbonate by exposure to a stream of dry carbonic anhydride; the carbonate is washed with anhydrous ether, and dissolved in hydrochloric acid; and the crystallised hydrochlorate is decomposed with potash as above.

Benzylamine, thus prepared, is a colourless liquid, not altered by light, and boiling at 182°—183°. (Toluidine, described, at vol. i. p. 575, as benzylamine, is crystalline at ordinary temperatures, and melts at · °). It mixes with water in all proportions (toluidine is but slightly soluble in cold water), and is separated therefrom by potash, with faint yellowish colour. It absorbs carbonic anhydride rapidly, forming a crystalline compound; has a strong alkaline reaction; forms white fumes with hydrochloric acid, and unites with acids, producing rise of temperature. Altogether, it appears to be a stronger base than toluidine.—*Hydrochlorate of benzylamine*, $C^7H^9N.HCl$, crystallises in striated tables; the *chloroplatinate* in orange-coloured laminæ.

Dibenzylamine, $(C^7H^7)^2HN$, isomeric with benzyltoluidine, has not been isolated, but appears to be formed, together with mono- and tri-benzylamine, in the process above described.

Tribenzylamine, $(C^7H^7)^3N$, isomeric with dibenzyltoluidine (p. 866), has been already described (i. 574).

Phenyl-benzylamine, $C^{13}H^{13}N = \left.\begin{matrix}C^6H^5\\ C^7H^7\\ H\end{matrix}\right\}N$. (Fleischer, Ann. Ch. Pharm. cxxxviii. p. 225; Bull. Soc. Chim. [1866], ii. 235.)—This base, isomeric with Hofmann's tolylaniline (iv. 454), is produced by mixing aniline with benzylic chloride (boiling at 170°).* The mixture becomes hot, and deposits white crystals, consisting of hydrochlorate of aniline, together with phenyl-benzylamine:

$$C^7H^7Cl + 2C^6H^7N = C^6H^7N.HCl + C^{13}H^{13}N.$$

The mixture must be heated to 160° for twenty-four hours, to complete the reaction; and on dissolving out the hydrochlorate of aniline from the product by water, the phenyl-benzylamine remains as an oil, which is converted by hydrochloric acid into crystals of the hydrochlorate, $C^{13}H^{13}N.HCl$. On decomposing this salt with soda, and distilling the liberated base under a pressure of 45 millimetres, the greater part passes over, between 200° and 220°, in the form of an oily liquid, which solidifies at a low temperature, and may be purified by pressure between bibulous paper, and recrystallisation from boiling alcohol.

Phenyl-benzylamine crystallises in colourless four-sided prisms, insoluble in water, but soluble in alcohol and in ether. It melts at 32°, remains in a state of surfusion at 12°, and boils under the ordinary pressure at a temperature above 310°. (Tolylaniline melts at 87°, and boils at 334°).—The *hydrochlorate*, $C^{13}H^{13}N.HCl$, forms colourless crystals.—The *oxalate*, $(C^{13}H^{13}N)^2.C^2H^2O^4$, forms white laminæ.—The base forms, with *chloride of cadmium*, the compound $C^{13}H^{13}N.CdCl^2$.

Phenyl-benzylamine, fused with mercuric chloride, forms at first a green mass, which dissolves in alcohol with fine blue colour; but by the prolonged action of heat, this mass assumes a dark colour, and then forms with alcohol a crimson solution.

Phenyl-benzylamine treated with *chloride of benzoyl* forms phenyl-benzyl-benzamide, $(C^6H^5)(C^7H^7)(C^7H^5O)N$, which crystallises in oblique prisms.

TOLUOL. Syn. with TOLUENE.

TOLUOLIC ACID. Syn. with TOLUIC ACID.

TOLUONITRILE. Syn. with BENZYLCYANIDE (i. 573).

TOLUOSALICYL, or **TOLUOSALICYLOL.** See SALICYLOL (p. 170).

TOLUOXYL. C^8H^7O.—The radicle of toluic acid and its derivatives. (Footnote, p. 869.)

TOLURIC ACID. $C^{10}H^{11}NO^3 = \left.\begin{matrix}H\\ (C^2H^2O)''\\ C^8H^7O\\ H\end{matrix}\right\}\begin{matrix}N\\ O\end{matrix}$.—*Toluglycic Acid. Glycocol-toluic Acid.* (Kraut, Ann. Ch. Pharm. xcviii. 360.)—An acid homologous with

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* Chlorotoluene (according to Fleischer), but the boiling-point shows that the compound used was really benzylic chloride (p. 85[illegible]).

the suborder *Cichoraceæ*, contains, according to Sprengel (J. f. techn., Chem. viii. 363), in 100 pts. of the fresh plant, 79·0 water, 19·9 organic substance, and 1·10 ash. The ash free from carbonic acid contains, in 100 pts.:

K^2O.	Na^2O.	CaO.	MgO.	Al^2O^3.	Fe^2O^3.	Mn^2O^3.	SiO^2.	SO^3.	P^2O^5.	Cl.
24·6	2·4	33·9	7·4	1·4	0·3	0·2	3·9	8·6	9·8	7·4

TRANSPIRATION. A term applied by Graham to the passage of gases and liquids through capillary tubes. (See GASES, ii. 820; and LIQUIDS, iii. 722.)

TRANSUDATION. A physiological term, denoting the passage of liquids from the bloodvessels, without laceration or perforation, into closed or open cavities of the body, into the parenchyma of the organs, or sometimes on to the surface of the body. (See SEROUS FLUIDS, p. 235.)

TRAP. A geological term, which was applied to melaphyre, basalt, dolerite, diabase, gabbro, &c., and generally to more or less compact, dark-coloured, eruptive rocks, before the several species were distinguished according to their constituents. *Trap-porphyry* is an old name for the so-called greenstone-porphyries, melaphyres, and phonolites.

TRAPA. The mineral constituents of this water-plant and of the water of a pond near Nürnberg, in which it grows, have been examined by Gorup-Besanez (Ann. Ch. Pharm. cxviii. 220; Jahresb. 1861, p. 751).—A is the composition of the ash of the plant gathered in June (stem-leaves, radical leaves, and roots); B, that of the plant gathered in May; C that of the fruit (the whole in percentages, after deduction of charcoal and sand); D, the composition, in 100 pts., of the ignited water-residue (amounting to 0·8044 pt. in 10,000 pts. of water):

	Ash per cent.	SiO^2.	Fe^2O^3	Mn^3O^4.	CaO.	MgO.	K^2O.	Na^2O.	Cl.	SO^3.
A.	15·92	27·34	23·40	14·70	17·65	5·15	6·06	2·71	0·46	2·53
B.	29·46	28·66	29·62	7·57	14·91	7·56	6·89	1·41	0·65	2·73
C.	7·75	4·84	68·60	9·63	9·77	0·91	1·26	0·62	0·41	3·92
D.	. .	1·90	1·11	0·15	42·24	18·08	9·07	9·21	1·18	17·03

From the considerable proportion of iron- and manganese-oxides in the ash of the plant, and from the different proportions of the several constituents in the plant-ash and in the water, Gorup-Besanez concludes that water-plants possess the power of selecting the constituents of the nutritive matters presented to them.

TRASS. A volcanic mass resembling pumice, and containing silicates decomposable by slaked lime, so that it is available for the preparation of cements. (See SILICATES OF CALCIUM, p. 251.)

TRAVERSELLITE. A name applied by Scheerer (Pogg. Ann. xciii. 109) to certain pseudomorphs of hornblende after augite (regarded by him as paramorphs, iv. 350), occurring at Traversella in Piedmont. These pseudomorphs are remarkable for retaining the form of the augite crystals, while the substance, in consequence of the transformation, has acquired a fibro-crystalline structure, so that the augitic crystals are made up of parallel fibres.

TRÆVERTINO. Calcareous tufa, occurring at Tivoli, Viterbo, Ascoli, and other places in Central Italy.

TREHALA, or **TRICALA.** A substance imported from Persia, and consisting of the hollow cocoons of a coleopterous insect (*Larinus maculatus*). The larva of this insect eats the branches of *Echinops persica*, for the sake of the sugar, starch, and gum contained in them, and afterwards voids these substances to form its cocoon. The organic portion of trehala consists, according to Guibourt (J. Pharm. [3], xxxiv. 81; Jahresb. 1858, p. 485), of 66·5 per cent. starch, 4·6 sparingly soluble gum, 28·9 sugar, and bitter principle. The sugar, called trehalose, appears to be identical with the mycose of ergot-of-rye (iii. 1698). The starch differs from that of the potato, being more like that of sago, or still more like the insoluble portion of gum-tragacanth. Trehala yields 4·6 per cent. ash, of which 3 pts. are soluble in water, and consist of alkaline carbonates, sulphates, and chlorides, with small quantities of phosphate; 1·4 pts. insoluble, consisting chiefly of calcic carbonate with a little ferric phosphate; and 0·2 sand. Trehala has a sweetish taste, swells up in water, and is converted into a thick mucilaginous paste.

TREHALOSE. See MYCOSE (iii. 1068).

TREMELLA. A genus of gelatinous algæ. *Tr. mesenterica* was found by Brandes to contain, in the dry state, 84 pts. of a substance which swelled up in water, and 5 pts. of a peculiar crystallisable resinous body, called tremellin, but not further investigated. *Tr. Nostoc* contains, in the fresh state, 97 per cent. water and 2·5 dry substance; the ash consists mainly of potassium-salts. (Braconnot.)

TREMENHEERITE. A name given by Piddington to a black, scaly, metallically lustrous mineral, probably an impure graphite, containing 85·7 per cent. carbon, together with earthy matters, sulphide of iron, and water. (Dana, ii. 30.)

TREMOLITE. A subspecies of hornblende (iii. 169).

TRI. In this Dictionary the syllable *tri*, prefixed to the name of a radicle occurring in any compound, denotes that the compound in question contains three atoms of that radicle: *e.g.*, trichloride of bismuth = $BiCl^3$; trioxide of antimony, Sb^2O^3; trisodic phosphate, Na^3PO^4; triethylamine, $(C^2H^5)^3N$, &c. The prefix *ter* is often used in the same sense. (See NOMENCLATURE, iv. 125, 127.)

Individual tri-compounds are, for the most part, described under the several general headings: e. g., *trichloride of bismuth* under BISMUTH, CHLORIDES OF; *trisodic phosphate* under PHOSPHATES OF SODIUM; *triethylamine* under ETHYLAMINES, &c.

TRIALLYL-SULPHIODIDE. $(C^3H^5)^3SI$. *Triallylsulfiniodür.*—This compound is obtained by heating allylic sulphide with methylic iodide in prismatic crystals, soluble in water, and forming an alkaline liquid with silver-oxide. (Cahours, Jahresb. 1865, p. 476.)

TRIAMYL-GLYCERIN, $C^{18}H^{38}O^3 = \left.\begin{matrix}(C^3H^5)'''\\(C^5H^{11})^3\end{matrix}\right\}O^3$, appears to be produced by heating 1 vol. acrolein, 3 vols. amylic alcohol, and 0·5 vol. acetic acid, to 110° for twelve hours. It is decomposed by distillation. (Alsberg, Jahresb. 1864, p. 495.)

TRIAMYLIDENE. See TRIOXAMYLAMINE.

TRIANOSPERMA. In the root of *Trianosperma ficifolia*, a climbing cucurbitaceous plant, indigenous in Brazil, Peckholt (Arch. Pharm. [2], cxiii. 104) found a drastic bitter principle (*toguyin*), a small quantity of a body slightly soluble in alcohol and water, insoluble in ether, and crystallising in pointed needles (*trianospermin*), and another (*trianospermitin*), crystallising in white grains, soluble in ether, but insoluble in alcohol and in water, besides several resins.

TRICALA. Syn. with TREHALA (p. 878).

TRICAPRONYLAMINE. See TRIŒNANTHYLAMINE.

TRICARBALLYLIC ACID. $C^6H^8O^6 = \left.\begin{matrix}(C^6H^5O^3)'''\\H^3\end{matrix}\right\}O^3$. Maxwell Simpson, Proc. Roy. Soc. xii. 236; xiv. 77; Chem. Soc. J. xviii. 331.—Wichelhaus, Ann. Ch. Pharm. cxxxii. 60.—Hlasiwetz, Zeitschr. Ch. Pharm. 1864, p. 734; Jahresb. 1864, p. 395.)—A tribasic acid, formerly called *carballylic acid*, discovered by Maxwell Simpson, who obtained it by the action of potash upon allylic tricyanide:

$$C^3H^5(CN)^3 + 3KHO + 3H^2O = C^6H^5K^3O^6 + 3NH^3.$$

Dessaignes (Compt. rend. lv. 510), by treating aconitic acid with sodium-amalgam, obtained a peculiar acid, which, however, he did not succeed in preparing in the pure state; and this acid has been shown by Wichelhaus to be identical with tricarballylic acid. Lastly, Hlasiwetz has obtained the same acid by the action of sodium-amalgam on aconitic ether.

Preparation.—1. From Allylic tricyanide.—1 at. allylic tribromide and 3 at. pure potassium cyanide are heated to 100° in a closed flask for sixteen hours with a large quantity of alcohol, and the decanted alcoholic solution is boiled with potassium-hydrate as long as ammonia is evolved. The alcohol is then distilled off; the remaining potassium-salt decomposed by nitric acid; the dried mass exhausted with alcohol; and the acid remaining after evaporation of the alcohol, first converted into an ammonium-salt, then into the less soluble silver-salt. By decomposing the latter with sulphydric acid, the tricarballylic acid is obtained pure (Simpson).—2. From Aconitic acid.—The sodium-salt obtained by the action of sodium-amalgam on aconitic acid is precipitated with acetate of lead; the washed precipitate is decomposed with sulphydric acid; the acid thereby liberated, is repeatedly crystallised, and then converted into a silver-salt, to free it from obstinately adhering resinous substance, and this salt is decomposed by sulphydric acid (Wichelhaus).—When ethylic aconitate is mixed with a quantity of sodium-amalgam (containing 0·8 per cent. sodium), sufficient to form a thick unctuous mass, the mixture being cooled from time to time, and this mass is treated with ether, the ethereal solution boiled with potash, then neutralised and precipitated with acetate of lead, a lead-salt is obtained, which, when decomposed by sulphydric acid, yields tricarballylic acid. (Hlasiwetz.)

Properties.—Tricarballylic acid forms colourless crystals, which (according to Miller's determination) are trimetric, and exhibit the combination $\infty\breve{P}\infty \,.\, \infty P \,.\, \frac{1}{2}\breve{P}\infty \,.\, \infty\breve{P}2 \,.\, 2\breve{P}2$. Angle $\infty\breve{P}\infty : \frac{1}{2}\breve{P}\infty = 113° 34'$; $\frac{1}{2}\breve{P}\infty : \frac{1}{2}\breve{P}\infty = 131° 52'$; $\infty\breve{P}\infty$

$: \infty P = 134° 0'; \infty P : \infty P = 92° 0'; \infty\breve{P}\infty : \infty\breve{P}2 = 152° 38'; \infty\breve{P}\infty : 2\breve{P}2 = 142° 19'; \infty P : 2\breve{P}2 = 147° 37'; \infty\breve{P}2 : 2\breve{P}2 = 153° 1'$. The crystals cleave perfectly parallel to $\infty\breve{P}\infty$. The acid is easily soluble in water and in alcohol, sparingly soluble in ether, and has an agreeably acid taste. It resembles succinic acid in not being decomposed by nitric acid, and in forming, after neutralisation, a red-brown precipitate with ferric chloride; but it is distinguished from that acid by melting at 158°, and decomposing at a higher temperature. (Simpson.)

Tricarballylates.—The neutralised solution of the acid gives precipitates with the chlorides of barium and calcium only after addition of alcohol.—The *barium-salt*, $C^{12}H^{10}\overset{''}{Ba}{}^3O^{12}.6H^2O$, gives up its water at 130° (Hlasiwetz).—The *calcium-salt*, $C^{12}H^{10}\overset{''}{Ca}{}^3O^{12}.4H^2O$, is a white, amorphous, slightly soluble powder.—The *cupric salt*, $C^{12}H^{10}\overset{''}{Cu}{}^3O^{12}$, is a bluish-green, the *lead-salt*, $C^{12}H^{10}\overset{''}{Pb}{}^3O^{12}$, a white precipitate. The aqueous solution of the acid, boiled with recently precipitated *mercuric oxide*, yields a filtrate, which on evaporation deposits white crystals, having a silvery lustre.—The *silver-salt* contains $C^6H^5Ag^3O^6$.—The *sodium-salts* of tricarballylic acid are easily soluble, and difficult to crystallise.—The *disodic salt* has probably the composition $C^6H^6Na^2O^6.2H^2O$. (Simpson.)

TRICARBALLYLIC ETHERS. The *ethylic ether*, $\left.\begin{matrix}C^6H^5O^3\\(C^2H^5)^3\end{matrix}\right\}O^3$, is formed by passing hydrochloric acid gas into a solution of tricarballylic acid in absolute alcohol, and distilling the product, after freeing it from excess of alcohol. It is a colourless liquid, boiling between 295° and 305°, slightly soluble in water, and having a sharp taste. (Simpson.)

The *amylic ether*, $\left.\begin{matrix}(C^6H^5O^3)'''\\(C^5H^{11})^3\end{matrix}\right\}O^3$, prepared in like manner, is a heavy oily liquid, having a sharp taste, and a very high boiling-point. (Simpson.)

Glycerin-tricarballylic acid, $\left.\begin{matrix}(C^6H^5O^3)'''\\(C^3H^5)'''\\H^4\end{matrix}\right\}O^5$?, is formed by heating tricarballylic acid with twice its weight of glycerin to 200° for several hours. On neutralising the product with baryta, and treating the salt left on evaporation with absolute alcohol, to remove the excess of glycerin, a barium-salt is obtained, which appears to have the composition $\left.\begin{matrix}(C^6H^5O^3)'''\\(C^3H^5)'''\\Ba''H^2\end{matrix}\right\}O^6$. (Simpson.)

TRICHALCITE. $\overset{''}{Cu}{}^3As^2O^8.5H^2O$.—A cupric arsenate, allied to tyrolite, occurring in stellate groups and dendritic crusts on fahl-ore at an unnamed locality in Siberia.

It has a verdigris-green colour and silky lustre; hardness = 2. When heated in a tube, it decrepitates very strongly, gives off a large quantity of water, and becomes dark-brown. The dehydrated mineral melts to a bead on charcoal, in the outer blowpipe-flame; in the inner flame it gives off arsenic vapours, and is reduced to granules of copper. It dissolves easily and completely in hydrochloric and in nitric acid, without evolution of gas. (R. Hermann, J. pr. Chem. lxxiii. 212.)

TRICHOPYRITE. Syn. with CAPILLARY PYRITES or NATIVE SULPHIDE OF NICKEL (iv. 42).

TRICLASITE. Syn. with FAHLUNITE (ii. 615).

TRIDACIUM. Syn. with THRIDACIUM (p. 788).

TRIDECYL, HYDRIDE OF. $C^{13}H^{28} = C^{13}H^{27}.H$. *Hydride of Cocinyl.*—A hydrocarbon of the marsh-gas series, occurring in American petroleum. It boils at 216°—218°, has a strong turpentine-like odour, burns with a very smoky flame, and is converted by chlorine into chloride of tridecyl, $C^{13}H^{27}Cl$. (Pelouze and Cahours, Jahresb. 1863, p. 530.)

TRIETHYLGLYCERIN, or **TRIETHYLIN.** $C^9H^{20}O^3 = \left.\begin{matrix}(C^3H^5)'''\\(C^2H^5)^3\end{matrix}\right\}O^3$. — This compound, which Reboul and Lourençço obtained by treating diethyl-chlorhydrin with sodium-ethylate (ii. 884), is likewise produced by heating 1 vol. acrolein, 1 vol. alcohol, and 0·5 vol. acetic acid to 100°; also, in small quantity, by gently heating a mixture of acrolein and alcohol saturated with sulphurous acid gas; but in this case brown resinous products are likewise formed.

Triethylin is a liquid having a pleasant ethereal odour, somewhat soluble in water, boiling at 186°, and of specific gravity 0·8955 at 15°. (Alsberg, Jahresb. 1865, p. [illegible]5.)

TRIETHYLSULPHINE. See the next article.

TRIETHYLSULPHUROUS COMPOUNDS. (A. v. Oeffele, Chem. Soc. J. xvii. 106; Ann. Ch. Pharm. cxxxii. 82; Jahresb. 1864, p. 478.—Cahours, Ann. Ch. Pharm. cxxxv. 352; cxxxvi. 151; Jahresb. 1865, p. 476.—Dehn, Ann. Ch. Pharm. Suppl. iv. 83; Jahresb. 1865, p. 479.)—Ethylic monosulphide, $(C^2H^5)^2S$, and ethylic iodide, when heated together, unite and form triethylic sulphiodide, $(C^2H^5)^3SI$; this compound, decomposed by moist oxide of silver, yields the corresponding hydroxylate, $(C^2H^5)^3S(HO)$; and from this, which is a strong base, the corresponding chloride, sulphate, nitrate, &c., may be prepared in the usual way. (v. Oeffele.)

Bromide and chloride of ethyl unite, in like manner, with ethylic sulphide, but less readily than the iodide. (Cahours.)

Triethylic sulphiodide is also produced by the action of ethylic iodide on ethylic sulphydrate (mercaptan), or of hydriodic acid on ethylic sulphide (Cahours), thus:

$$C^2H^5.H.S + 2C^2H^5I = (C^2H^5)^3SI + HI.$$
$$2(C^2H^5)^2S + HI = (C^2H^5)^3SI + C^2H^5.H.S.$$

Triethylic sulphobromide is further produced, together with other sulphobromides of ethyl and ethylene, by heating ethylic sulphide with ethylenic bromide and water, the reaction taking place by several stages, as follows:

$$\underset{\substack{\text{Ethylic}\\\text{sulphide.}}}{(C^2H^5)^2S} + \underset{\substack{\text{Ethylenic}\\\text{bromide.}}}{C^2H^4Br^2} = \underset{\substack{\text{Ethylenic}\\\text{sulphide.}}}{(C^2H^4)S} + \underset{\substack{\text{Ethylic}\\\text{bromide.}}}{2C^2H^5Br.}$$

$$\underset{\substack{\text{Ethylenic}\\\text{sulphide.}}}{C^2H^4S} + \underset{\substack{\text{Ethylenic}\\\text{bromide.}}}{C^2H^4Br^2} = \underset{\substack{\text{Ethylenic}\\\text{sulphodibro-}\\\text{mide.}}}{(C^2H^4)^2SBr^2.}$$

$$\underset{\substack{\text{Ethylic}\\\text{sulphide.}}}{(C^2H^5)^2S} + \underset{\substack{\text{Ethylic}\\\text{bromide.}}}{C^2H^5Br} = \underset{\substack{\text{Triethylic}\\\text{sulphobro-}\\\text{mide.}}}{(C^2H^5)^3SBr.}$$

$$\underset{\substack{\text{Ethylic}\\\text{sulphide.}}}{(C^2H^5)^2S} + \underset{\substack{\text{Ethylenic}\\\text{bromide.}}}{C^2H^4Br^2} = \underset{\substack{\text{Ethylene-diethylic}\\\text{sulphodibromide.}}}{(C^2H^4)(C^2H^5)^2SBr^2.}$$

The mode of separating these products will be described further on.

The constitutions of these triethylic sulphur-compounds may be represented in three different ways. The iodide, for example, may be regarded:

α. As triethylic sulphiodide, $(C^2H^5)^3\left\{\begin{matrix}S''\\I\end{matrix}\right.$.

β. As iodide of triethylsulphine, $(C^2H^5)^3S'''.I.$

γ. As sulphurous triethiodide, $S^{iv}\left\{\begin{matrix}(C^2H^5)^3\\I\end{matrix}\right.$.

In the first of these formulæ the sulphur is diequivalent, in the second triequivalent, and in the third tetraequivalent, as in sulphurous acid, $\left.\begin{matrix}S^{iv}\\H^2\end{matrix}\right\}O^3$. The last is, perhaps, the most probable view of the constitution of these bodies.

In the ethylenic sulphodibromide, obtained by Dehn, in the manner above mentioned, the sulphur may, in like manner, be regarded as hexequivalent, as in sulphuric acid; thus:

$$(C^2H^4)^2SBr^2 = \text{Sulphuric Diethylene-dibromide, } S^{vi}\left\{\begin{matrix}(C^2H^4)''\\(C^2H^4)''.\\Br^2\end{matrix}\right.$$

$$(C^2H^4)(C^2H^5)^2SBr^2 = \text{Sulphuric Ethylene-diethyldibromide, } S^{vi}\left\{\begin{matrix}(C^2H^4)''\\(C^2H^5)^2.\\Br^2\end{matrix}\right.$$

Sulphurous Bromotriethide, $S(C^2H^5)^3Br$.—This compound is produced, as above stated, by heating 1 at. ethylic sulphide with 1 at. ethylic bromide, to 130°—140°, for eight or ten hours. It crystallises in colourless rhombic needles, is extremely soluble in water, sparingly soluble in alcohol, insoluble in ether. (Cahours; Dehn.)

Sulphurous Chlorotriethide, $S(C^2H^5)^3Cl$.—Ethylic chloride heated to 100° for sixty hours with ethylic sulphide yields only traces of this compound (Cahours). Dehn prepares it from the mixture of products obtained by heating ethylic sulphide with ethylenic bromide (*supra*) as follows:—The watery portion of the product, containing sulphurous bromotriethide, sulphuric dibromo-diethylenide, and sulphuric dibromo-ethylene-diethide, is separated from the oily layer (containing diethylenic sulphide), and evaporated; the residue is redissolved in water; the filtrate digested with recently-precipitated silver-oxide, and a small quantity of silver-sulphide; and the liquid (freed from silver and sulphuric acid) is supersaturated with hydrochloric acid, concentrated, and fractionally precipitated with platinic chloride. The first scanty precipitates thereby obtained consist of the chloroplatinates of sulphuric dichloro-diethylenide, $S(C^2H^4)^2Cl^2.PtCl^4$, and sulphurous dichloro-ethylene-diethide, $S(C^2H^4)(C^2H^5)^2Cl^2.PtCl^4$; finally, the chloroplatinate of sulphurous chlorotriethide crystallises out; and this salt, decomposed by sulphydric acid, yields sulphurous chlorotriethide.

Sulphurous chlorotriethide volatilises with vapour of water, deliquesces in moist air, is insoluble in ether, very slightly soluble in alcohol, and crystallises from a syrupy aqueous solution in white needles. It unites with metallic chlorides.—The *chloromercurate*, $S(C^2H^5)^3Cl.4HgCl^2$, crystallises in needles or laminæ, which dissolve in 65·8 pts. water at 20° (or in 8 pts. at 80°), melt and partially sublime at a temperature a little above 100°.—The *chlorostannate* is a very soluble salt, crystallising in needles. (Dehn.)

The *chloroplatinate*, $2S(C^2H^5)^3Cl.PtCl^4$, prepared as above, crystallises from a hot saturated solution in small light red needles, and by slow cooling of a warm non-saturated solution in garnet-red, well-developed crystals, which (according to A. Knop's determination) are monoclinic, and usually exhibit the combination $\infty P . oP . \infty P\infty . +P\infty$, the last two faces being subordinate, and sometimes wanting, whereby the crystals acquire a rhombohedral character. Ratio of axes, $a : b : c = 0·6745 : 1 : 1·1068$. Angle $b : c = 55° 6'$; $\infty P : \infty P$ (clinod.) $= 78° 52'$; $\infty P : oP = 68° 40'$ and $111° 20'$; $oP : +P\infty = 152° 0'$; $\infty P : \infty P\infty = 129° 36'$. The crystals melt at about 170°, dissolve in 30 pts. water at 20°, in 3 to 4 pts. at 100°, are nearly insoluble in alcohol, and quite insoluble in ether. (Dehn.)

Sulphurous Hydroxyltriethide, $S^{iv}\left\{\begin{matrix}(C^2H^5)^3\\HO\end{matrix}\right.$, or *Hydrate of Triethylsulphine*, $(C^2H^5)^3S.HO$, prepared by agitating or boiling the iodide with recently-precipitated silver-oxide, forms a strongly alkaline solution, which quickly absorbs carbonic acid, precipitates metallic salts like hydrate of potassium, and dries up over oil of vitriol to a crystalline, extremely deliquescent mass (v. Oeffele). According to Dehn, it dissolves the skin like caustic potash, eliminates ammonia from its salts when warmed with them, emitting at the same time a slight odour of ethylic sulphide: forms a green precipitate with cupric sulphate, black at the boiling heat; white with zinc-sulphate and lead-acetate, the precipitate in either case being insoluble in excess; with alum, &c. it forms a gelatinous precipitate, easily soluble in excess.

Sulphurous Iodotriethide, $S(C^2H^5)^3I$, is prepared by heating equivalent quantities of ethylic sulphide and iodide to 105°—110°; or 1 at. mercaptan, 2 at. ethylic iodide, and 1 at. absolute alcohol to 140°. It separates from alcoholic solution in small crystals, belonging to the trimetric system, and exhibiting the combination $\infty\bar{P}\infty . \bar{P}\infty . \breve{P}\infty . \infty P$, often tabular from predominance of $\infty\bar{P}\infty$, and with the faces $\breve{P}\infty$ generally occurring hemihedrally. The salt dissolves easily in water and in hot alcohol, but is nearly insoluble in ether; when heated above 100°, it melts, and decomposes into ethylic sulphide and iodide, without separation of iodine.—When the ether-alcoholic mother-liquor remaining in the preparation of the iodide, and containing a large quantity of free iodine, is shaken up with mercury, the compound $S(C^2H^5)^3I.HgI^2$ is formed, and crystallises from alcohol in light-yellow needles or laminæ, sparingly soluble in water. (Dehn.)

Sulphurous Nitratotriethide, $S^{iv}\left\{\begin{matrix}(C^2H^5)^3\\NO^3\end{matrix}\right.$, or *Nitrate of Triethylsulphine*, $(C^2H^5)^3.SNO^3$, obtained by treating the hydrate with nitric acid, forms deliquescent needles, uniting in radiate laminæ; it combines with nitrate of silver, forming the scaly double salt, $S(C^2H^5)^3(NO^3).AgNO^3$, sparingly soluble in cold water and in alcohol.

Sulphurous Sulphatotriethide, $\overset{''''}{S}{}^2\left\{\begin{matrix}(C^2H^5)^6\\(SO^4)''\end{matrix}\right.$, or *Sulphate of Triethylsulphine*, $[(C^2H^5)^3S]^2.SO^4$, obtained by decomposing the chloride with silver-sulphate, forms indistinct crystalline aggregates, easily soluble in water, sparingly in alcohol.

Acetate.—When sulphurous bromotriethide is decomposed with acetate of lead, and the filtrate freed from lead by sulphydric acid, crystalline crusts are formed, which separate from alcohol covered with a layer of ether, in large crystals containing bromine—perhaps a compound of sulphurous bromotriethide with sulphurous acetotriethide; and by completely removing the bromine with acetate of silver, the acetotriethide, or acetate of triethylsulphine, $(C^2H^5)^3S(C^2H^3O^2)$, is obtained as a gummy mass, slightly soluble in absolute alcohol, and precipitated therefrom in flocks by ether. (Dehn.)

Sulphurous Iodomethodiethide and *Iodo-amyldiethide* are obtained, like sulphurous iodotriethide, by heating ethylic sulphide with methylic or amylic iodide. The former, treated with silver-oxide, yields a deliquescent hydrate; and from this a platinum-salt may be obtained, crystallising in needles, and containing $2CH^3(C^2H^5)^2SCl.PtCl^4$. (Cahours; Dehn.)

TRIETHYL-TRITYLPHYCITE. See Tritylphycite (p. 895.)

TRIFOLIUM. The ash of three species of this genus, used as fodder for cattle—viz., *Tr. pratense*, common clover (I.), *Tr. pratense perenne* (II.), and *Tr. medium* (III.)—has been analysed by Way and Ogston (Roy. Agr. Soc. J. xi. [2], 536; Jahresb. 1850, p. 668), with the following results:

	I.	II.	III.
Water, in 100 pts. of air-dried substance . . .	81·0	81·0	78·6
Ash per cent. in dry substance	9·56	8·45	7·97
Sulphur per cent. in dry substance	0·27	0·10	0·20

Composition of the Ash in 100 *pts.*

	K^2O.	Na^2O.	CaO.	MgO.	Fe^2O^3.	SO^3.	SiO^2.	CO^2.	P^2O^5.	KCl.	NaCl.
I.	36·4	. .	22·6	4·1	0·2	1·8	0·6	23·5	6·7	2·4	1·5
II.	22·1	2·8	26·6	10·2	0·3	2·1	1·1	22·7	8·5	. .	3·4
III.	34·7	. .	24·5	4·5	0·2	1·1	0·6	25·5	5·4	0·8	2·5

Way (Roy. Agr. Soc. J. xiv. [1], 171), has also determined the percentage composition of the following species:

	Water.	Albumin.	Fat.	Sugar.	Cellulose.
Tr. pratense	81·0	4·3	0·69	8·4	3·7
Tr. pratense perenne . . .	81·0	3·6	0·78	8·0	4·9
Tr. incarnatum	82·1	2·9	0·67	6·7	5·8
Tr. medium	74·1	6·3	0·92	9·4	6·2
Tr. procumbens	83·5	3·4	0·77	7·2	3·7
Tr. repens	79·7	3·8	0·89	8·1	5·4

Völcker (Scott. Agr. Soc. J., July 1853), gives the following composition: No. I. for *Tr. pratense* (red clover); No. II. for *Tr. repens* (white clover); No. III. for *Tr. hybridum* (Alsike clover):

	I.	II.	III.
Water	80·6	83·6	76·7
Nitrogenous substance . .	3·6	4·5	4·8
Non-nitrogenous substance .	13·8	10·2	16·4
Ash	2·0	1·6	2·0

100 pts. of the dry seed of *Tr. pratense* give 4·68 pts. ash, of which 1·21 is soluble in water, 3·19 soluble in hydrochloric acid, and 0·28 consists of silica; 14·5 grms. of the air-dried plant of *Tr. pratense* grown in sand yielded 0·96 grm. ash, and the same quantity of the plant grown in artificial soil yielded 1·6 grm. ash, containing respectively:

	In sand.	In artificial soil.
Soluble in water	0·52	0·66
Soluble in hydrochloric acid .	0·35	0·94
Silica	0·09	0·08
	0·96	1·68

TRIGENIC ACID. $C^4H^7N^3O^2 = (CN)^2O.C^2H^3(NH^4)O$. (Wöhler and Liebig, Ann. Ch. Pharm. lix. 296.)—This acid, containing the elements of cyanic anhydride and aldehyde-ammonia, is obtained, together with other products, by passing the vapour of cyanic acid over aldehyde. The action is violent, and therefore, to avoid projection, only a few grammes of aldehyde should be used, and the vessel kept cool with ice. The mass soon enters into ebullition, giving off carbonic anhydride, and concretes into a thick substance, like calcined borax; frequently also a syrupy mass is obtained, in which crystalline crusts gradually form. This product contains trigenic acid, cyamelide, aldehyde-ammonia, and perhaps other accidental products. On dissolving it in moderately strong hydrochloric acid, boiling the solution as long as vapours of aldehyde continue to go off, and then filtering, the trigenic acid crystallises out on cooling; if yellow, it must be decolorised with animal charcoal. Its formation may be represented by the equation:

$$\underset{\text{Aldehyde.}}{C^2H^4O} + \underset{\text{Cyanic acid.}}{3CNHO} = \underset{\text{Trigenic acid.}}{C^4H^7N^3O^2} + CO^2.$$

Trigenic acid crystallises in small prisms, slightly soluble in water, nearly insoluble in alcohol. When subjected to dry distillation, it melts and carbonises, giving off alkaline vapours, which have the odour of chinoline, and appear to consist of that alkaloïd; cyanic acid is also produced.

Trigenic acid is not precipitated by nitrate of silver unless ammonia is also added, in which case *trigenate of silver*, $C^4H^6AgN^3O^2$, is precipitated in the form of a powder, appearing under the microscope to consist of crystalline spherules; when exposed to light, it acquires a violet tint. It dissolves in boiling water, and is deposited in the pulverulent state on cooling. Between 120° and 130° it gives off water, and becomes light-brown; and at 160° it melts, turning black, and giving off a thick vapour having the odour of chinoline.

TRIGLOCHIN. *Arrow-grass.*—A genus of plants belonging to the juncaginaceous order. *Tr. maritimum* contains, according to Sprengel (J. techn. Chem. v. 293; vi. 92), in 100 pts: 76·0 water, 20·7 organic substance, and 2·24 ash (I.). *Tr. palustre* contains 75·0 per cent. water, 22·7 organic substance, and 2·12 ash (II.). The ashes of these two plants contain, in 100 pts.:

	K^2O.	Na^2O.	CaO.	MgO.	Al^2O^3.	Fe^2O^3.	Mn^2O^3.	SiO^2.	Cl.	P^2O^5.	SO^3.
I.	17·7	22·3	10·0	2·2	0·2	1·7	. .	4·4	3·28	4·9	3·8
II.	13·7	20·7	14·6	3·9	0·2	0·4	1·5	5·1	13·0	0·6	26·1

The root of *Tr. maritimum* is said to yield a large quantity of starch.

TRIGLYCOLLAMIC ACID. See GLYCOLLAMIC ACIDS (ii. 905).

TRIHEPTYLAMINE. $(C^7H^{15})^3N$.—*Triœnanthylamine.* (Petersen and Gössmann, Ann. Ch. Pharm. ci. 310; cii. 312; Jahresb. 1857, p. 388.—Petersen, Ann. Ch. Pharm. cxxxii. 158; Jahresb. 1865, p. 420.)—This base, originally regarded as trihexylamine (tricapronylamine), is produced by heating sulphite of œnanthyl-ammonium with three times its weight of a mixture of quicklime and slaked lime:

$$3(C^7H^{15})(NH^4)SO^3 + 3CaO = (C^7H^{15})^3N + 2NH^3 + 3CaSO^4.$$

It is also formed by heating œnanthyl-ammonium-sulphite by itself to 260°—270° in a sealed tube. When purified by boiling with sodic carbonate, washing with water, and rectifying in a stream of hydrogen, it forms a liquid, pale-yellow by transmitted, greenish-yellow by reflected light, and strongly efflorescent; it has an alkaline reaction, a peculiar aromatic odour, and an alkaline aromatic taste, producing afterwards a scratching sensation in the throat. It is lighter than water, and nearly insoluble therein, easily soluble in alcohol and in ether. It precipitates alumina and ferric oxide from their salts, and redissolves them in excess; does not decompose ammonia-salts.

The base turns brown on exposure to the air; its salts are all deliquescent, easily alterable, and form oily drops or syrupy masses.—The *chloroplatinate*, $2C^{21}H^{46}NCl.PtCl^4$, separates from alcoholic solution, by evaporation in a vacuum, in yellow shining scales.

The base, left in contact for several weeks with ethylic iodide, or heated with it to 100° for 24 to 48 hours, forms a red oily mass, consisting of iodide of triheptyl-ethyl-ammonium, $(C^7H^{15})^3(C^2H^5)NI$.

TRIHEPTYLIDENE-DIROSANILINE. $C^{61}H^{74}N^6 = \left.\begin{matrix}(C^{20}H^{16})^2\\(C^7H^{14})^3\end{matrix}\right\}N^6 = \left.\begin{matrix}(C^6H^4)^2\\(C^7H^6)^4\\(C^7H^{14})^3\end{matrix}\right\}N^6$.—*Triœnanthylidene-dirosaniline.* (H. Schiff, Compt. rend. lxi. 45; Jahresb. 1865, p. 420.)—Produced as an acetate, by the action of œnanthol on crystallised acetate of rosaniline at ordinary temperatures, and separated by potash, from the blue alcoholic solution of that salt, in red crystalline flocks:

$$\underset{\text{Rosaniline.}}{2(C^{20}H^{16})H^3N^3} + \underset{\text{Œnanthol.}}{3C^7H^{14}O} = \underset{\text{Triheptylidene-dirosaniline.}}{(C^{20}H^{16})^2(C^7H^{14})^3N^6} + 3H^2O.$$

It forms crystalline copper-coloured salts, insoluble in water, and several platinum-salts. Both the base and its salts decompose even below 100°, especially in presence of excess of œnanthol, yielding a yellow resinous mass, consisting mainly of heptylidene-dibenzylidene-diamine, $C^{21}H^{26}N^2 = (C^7H^{14})(C^7H^6)^2N^2$. This compound scarcely exhibits basic properties, but nevertheless forms a yellow platinum-salt, $2(C^{21}H^{26}N^2.HCl).PtCl^4$. Its formation probably takes place in the manner represented by the equation:

$$\underset{\text{Triheptylidene-dirosaniline.}}{\left.\begin{matrix}(C^6H^4)^2\\(C^7H^6)^4\\(C^7H^{14})^3\end{matrix}\right\}N^6} = \underset{\text{Heptylidene-diphenylene-diamine.}}{\left.\begin{matrix}(C^6H^4)^2\\C^7H^{14}\end{matrix}\right\}N^2} + \underset{\text{Heptylidene-dibenzylidene-diamine.}}{2\left[\left.\begin{matrix}(C^7H^6)^2\\C^7H^{14}\end{matrix}\right\}N^2\right]}.$$

TRIHYDROCARBOXYLIC ACID. See HYDROCARBOXYLIC ACIDS (iii. 189).

TRIMERCURANIL, NITRATE OF. Syn. with NITRATE OF DIPHENYLTRIMERCURAMMONIUM. (See PHENYLAMMONIUMS, iv. 475.)

TRIMETHYL-GLYCERIN, or **TRIMETHYLIN,** $C^6H^{14}O^3 = \left.\begin{matrix}(C^3H^5)'''\\(CH^3)^3\end{matrix}\right\}O^3$, is formed by heating 1 vol. acrolein, 3 vols. methylic alcohol, and 0·5 vol. acetic acid, to 100° for several hours. It is a liquid having an agreeable odour, somewhat soluble in water, boiling at 148°, and having a specific gravity of 0·9433 at 0°. (Alsberg, Jahresb. 1865, p. 495.)

TRIMETHYLSULPHINE. See the next article.

TRIMETHYLSULPHUROUS COMPOUNDS. (Cahours, Ann. Ch. Pharm. cxxxvi. 151; Jahresb. 1865, p. 476.—Dehn, Ann. Ch. Pharm. Suppl. iv. 83; Jahresb. 1865, p. 479.)—These compounds are analogous in composition to the triethylsulphurous compounds above described (p. 881), and are obtained by similar reactions.

Sulphurous Iodotrimethide, $S^{iv}\left\{\begin{matrix}(CH^3)^3\\I\end{matrix}\right.$, or *Iodide of Trimethylsulphine,* $(CH^3)^3S.I$, is produced by direct combination of methylic sulphide, $(CH^3)^2S$, and methylic iodide, CH^3I; the two substances unite, at ordinary temperatures, to a white crystalline mass, which dissolves easily in hot water, and separates, by slow evaporation, in large prisms, quickly turning brown on exposure to light. The same compound is produced, together with methylic sulphydrate, by heating methylic sulphide with hydriodic acid in a sealed tube (Cahours):

$$2(CH^3)^2S + HI = (CH^3)^3SI + CH^3.H.S.$$

A mixture of methylic sulphocyanate and methylic iodide also solidifies on cooling to a crystalline mass consisting mainly of sulphurous iodotrimethide. This compound is slightly soluble in strong alcohol, insoluble in ether, and crystallises from aqueous alcohol in white needles, made up of small rhombic tablets. The aqueous solution is partly decomposed on evaporation, yielding methylic sulphide and free iodine. (Dehn.)

The iodide, decomposed with recently-precipitated silver-oxide, yields sulphurous hydroxyltrimethide, $S^{iv}\left\{\begin{matrix}(CH^3)^3\\HO\end{matrix}\right.$, or hydrate of trimethylsulphine, $(CH^3)SHO$, which is a strongly alkaline base, and, when neutralised with hydrochloric acid, yields the corresponding chloride in colourless deliquescent prisms.—The *chloroplatinate,* $2(CH^3)^3SCl.PtCl^4$, crystallises from hot water in sparingly soluble orange-yellow prisms.—The *chloroaurate* and *chloromercurate* also crystallise distinctly. The other salts, obtained by decomposing the iodide with silver-salts, are crystallisable and deliquescent (Cahours).—The *nitrate* forms, with nitrate of silver, a sparingly soluble double salt, which crystallises in needles. (Dehn.)

Sulphurous Iodo-ethyldimethide, $S^{iv}\left\{\begin{matrix}(CH^3)^2\\C^2H^5\\I\end{matrix}\right.$, is produced by the combination of methylic sulphide with ethylic iodide. (Cahours.)

Sulphurous Dibromodimethide, $S^{iv}\left\{\begin{matrix}(CH^3)^2\\Br^2\end{matrix}\right.$, is produced by adding bromine to methylic sulphide diffused through half its bulk of water, and treating the resulting reddish-yellow crystalline compound with a few drops of methylic sulphide. It is deliquescent, and separates from its colourless aqueous solution, by evaporation in a vacuum over oil of vitriol, in amber-yellow octahedral crystals. Moist silver-oxide converts it, at ordinary temperatures, into the corresponding oxide, $S(CH^3)^2SO$, which does not exhibit any alkaline reaction. (Cahours.)

Sulphurous Dibromo-ethylene-tetramethide, $\overset{iv}{S^2}\left\{\begin{matrix}(C^2H^4)''\\(CH^3)^4\\Br^2\end{matrix}\right.$, is produced, by heating 1 at. ethylenic bromide with 2 at. methylic sulphide to 100°, as a crystalline mass, which dissolves readily in water, and crystallises in a vacuum, in colourless well-defined crystals. It is deliquescent, is dissolved in all proportions by hot water, less easily by alcohol, is insoluble in ether, and is precipitated by ether from the alcoholic solution in white prisms. With silver-salts it yields silver-bromide, and very deliquescent salts; with recently-precipitated silver-oxide, a caustic alkaline solution, containing the oxide, $\overset{iv}{S^2}\left\{\begin{matrix}(C^2H^4)''\\(CH^3)^4\\O\end{matrix}\right.$.—The *chloroplatinate,* $(C^2H^4)(CH^3)^4S^2Cl^2.PtCl^4$, is orange-yellow and crystalline. (Cahours.)

Sulphurous Tribromo-ethenylhexmethide, $\overset{''}{S}{}^{3}\left\{\begin{matrix}(CH^{3})^{6}\\(C^{2}H^{3})'''\\Br^{3}\end{matrix}\right.$, is produced by combination of 3 at. methylic sulphide, $(CH^{3})^{2}S$, with 1 at. monobromethylenic bromide, $C^{2}H^{3}Br.Br^{2}$. It is crystallisable, deliquescent, and reacts with silver-oxide like the preceding. (Cahours.)

Iodoform dissolves easily in methylic sulphide, and crystallises out unaltered, on leaving the liquid to evaporate; but the mixture, if heated to 180°, turns brown, and deposits a dark-coloured crystalline mass, analogous in composition to the bromide last decribed. (Cahours.)

TRIMETHYL-TELLUROUS COMPOUNDS. (Cahours, *loc. cit.*)—*Tellurous iodotrimethide*, $Te^{iv}\left\{\begin{matrix}(CH^{3})^{3}\\I\end{matrix}\right.$, produced by direct combination of methylic telluride with methylic iodide, is crystalline, slightly soluble in water, easily soluble in alcohol. The alkaline base, obtained from it by the action of silver-oxide, yields, when neutralised with hydrochloric acid and treated with platinic chloride, a *chloroplatinate*, $2(CH^{3})^{3}TeCl.PtCl^{4}$, isomorphous with the corresponding sulphur-compound.

Similar compounds are formed with ethylic telluride and iodide; also with the corresponding selenides and iodides.

TRIMORPHISM. See DIMORPHISM (ii. 331).

TRINACRITE. A mineral from the palagonite tufa of Cape Passaro, in Sicily, in which it occurs mixed with siderosilicite. It contains 31·82 per cent. SiO^{2}, 33·95 $Fe^{2}O^{3}$, 5·26 $Al^{2}O^{3}$, 2·52 CaO, 4·57 MgO, 4·19 $Na^{2}O$, and 3·4 $K^{2}O$. (S. v. Waltershausen, *Vulcanische Gesteine*, p. 232.)

TRIŒNANTHYLAMINE. Syn. with TRIHEPTYLAMINE (p. 884).

TRIŒNANTHYLIDENE-DIROSANILINE. Syn. with TRIHEPTYLIDENE-DIROSANILINE (p. 884).

TRIOILITE. A name applied by Haidinger to the sulphide of iron, FeS, occuring in meteorites. (Jahresb. 1863, p. 905.)

TRIOXAMYLAMINE. $(C^{5}H^{11}O)^{3}N$. (J. Erdmann, Ann. Ch. Pharm. cxxx. 211; Jahresb. 1864, p. 420.)—A base produced by heating anhydrous valeral-ammonia, or a mixture of valeral and strong aqueous ammonia, to 130° in sealed tubes for six or eight hours:

$$3(C^{5}H^{10}O.NH^{3}) \;=\; (C^{5}H^{11}O)^{3}N \;+\; 2NH^{3}.$$

Erdmann designated this base as *triamylidenoxydammonia*, or *trioxamylidene*; the name and formula above given, which represent the base as analogous to hydrobenzamide, &c., were suggested by Petersen. (Ann. Ch. Pharm. cxxxii. 158.)

To obtain the pure base, the oily layer, which floats on the liquid when the reaction is completed, is distilled with water; the non-volatile portion, separated from the water, is dissolved in strong hydrochloric acid; and the hydrochlorate, $(C^{5}H^{11}O)^{3}N.HCl$, which separates from the solution in crystalline crusts, is washed with a little water, pressed between filter-paper, recrystallised from alcohol, washed with ether, and then shaken up with ammonia and ether. The resulting solution yields the base, on evaporation, as a colourless viscid oil, having a pungent odour when warm, and a specific gravity of 0·879 at 22°. It is partially decomposed by distillation, with evolution of ammonia, has a strong alkaline reaction, is but slightly soluble in water, easily soluble in alcohol, and, when once separated, unites but slowly with acids, forming crystallisable salts.—The *chloroplatinate*, $2(C^{15}H^{33}O^{3}N.HCl).PtCl^{4}$, is resinous, and crystallises from alcohol in yellowish-red granules.

Trioxamylamine, heated for several hours with *ethylic iodide*, is partially acted on, forming an iodide, which, when treated with silver-oxide, yields a very bitter alkaline base, obtainable in the form of a soft yellowish resin.

TRIOXYALIZARIN. Syn. with PSEUDOPURPURIN. (See PURPURIN, iv. 751.)

TRIOXYPROTEIN. See PROTEIN (iv. 738).

TRIPE-STONE. A variety of anhydrous calcic sulphate, composed of contorted plates.

TRIPHANE. Syn. with SPODUMENE (p. 403).

TRIPHYLLINE. Lithio-ferroso-manganous phosphate, $(Li^{2};Fe;Mn'')^{3}P^{2}O^{8}$. (See PHOSPHATES, iv. 572.)

TRIPLE SALTS. A name sometimes applied to salts containing three different bases, such as microcosmic salt, $Na(NH^{4})HPO^{4}$.

TRIPLITE. Ferroso-manganous phosphate. (See PHOSPHATES, iv. 571.)

TRIPOCLASE. Syn. with THOMSONITE (p. 784).

TRIPOLI. *Quarz aluminifère tripoléen. Argile tripoléenne. Terra tripolitana.*—A mineral consisting chiefly of silica, with small quantities of alumina, ferric oxide, and water, occurring massive in beds and nodules in various formations. Its structure is coarsely or finely earthy, sometimes rather slaty in the mass; of whitish, yellowish, greyish to blackish colour; sometimes spotted or striped; dull; opaque; somewhat rough to the touch; soft to friable, and of specific gravity 1·86 to 2·7. It may be regarded as an earthy variety of opal.

TRITHIONIC ACID. $H^2S^3O^6$. See SULPHUR, OXYGEN-ACIDS OF (p. 639).

TRITICIN. A name sometimes applied to the gluten of wheat.

TRITICUM. A genus of grasses including wheat. The rootstock of *Tr. repens* (couch-grass) is distinguished by its sweetish taste. Pfaff found in it a peculiar sugar, which Berzelius regarded as mannite. Stenhouse (Ann. Ch. Pharm. li. 354), by exhausting the extract of the plant with alcohol, obtained no mannite, but needle-shaped crystals of acid potassic oxalate, and an uncrystallisable, easily fermentable sugar. Völcker, however (*ibid.* lix. 380), has frequently observed the occurrence of mannite in the extract of couch-grass root; he found, indeed, that the extract of roots grown in the hot and dry summer of 1849, solidified almost entirely to a mass of needles of mannite. (Handw. d. Chem. viii. 1031.)

Respecting the composition of wheat (*Tr. vulgare*, &c.), and of its ash, see CEREALS (i. 824—828).

TRITOMITE. A hydrated silicate of cerium, lanthanum, calcium, &c., occurring in the syenite of the island of Lamö, near Brevig in Norway, in imbedded tetrahedrons exhibiting no distinct cleavage, but only a conchoïdal fracture. Hardness = 5·5. Specific gravity = 3·90 to 4·66. Colour brown to yellow; streak yellowish-grey. Lustre semi-metallic. Opaque or translucent on the edges only. When heated before the blowpipe, it often splits violently, swells up, and turns white. With borax, it forms a reddish-yellow bead, becoming colourless on cooling; when heated in a tube, it gives off water and fluorine. In the pulverulent state, it dissolves in hydrochloric acid, with evolution of chlorine and separation of gelatinous silica.

TRITOXIDE. A term formerly used to denote the third in a series of oxides, the first and second terms of which were called protoxide and deutoxide. (See NOMENCLATURE, iv. 123.)

TRITYL (better known as **PROPYL**) is the third radicle of the series C^nH^{2n+1}. Existing in combination, its formula is C^3H^7. In the free state it can hardly be said to be known as an actual substance, but, in accordance with received doctrines, its formula must be C^6H^{14}, and it is probably identical with the hydride of hexyl occurring in petroleum (iii. 153).

Isotrityl, or isopropyl, differs from propyl, and has been obtained by Schorlemmer (Proc. Roy. Soc. xvi. 35), by acting on iodide of isopropyl with sodium in presence of ether. It is a colourless mobile liquid, resembling the hexyl-hydride of petroleum in smell, but having a lower boiling-point, viz. 58°. Specific gravity at 10° = 0·6769. It is easily attacked by chlorine in the cold, yielding $C^6H^{13}Cl$. With chlorine and iodine it gives, not $C^6H^{13}Cl$, but $C^6H^{12}Cl^2$, and products still more highly chlorinated. Dilute chromic acid oxidises it to acetic and carbonic acids.

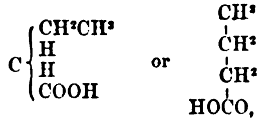
Isopropyl combines with alcohol-radicles when it is liberated nascent, in presence of the radicles also in the nascent state. Thus Schorlemmer (*loc. cit.*) obtained amylisopropyl, C^8H^{18}, a colourless liquid, boiling at 109°—110°, and of specific gravity 0·6980 at 16·5°, by attacking a mixture of iodide of amyl and iodide of isopropyl with sodium.

The difference in structure between normal trityl and isotrityl is expressed by the following formulæ:

Compound of normal trityl.	Compound of isotrityl.
$C\left\{\begin{array}{l}CH^2CH^3\\H\\H\\R\end{array}\right.$	$C\left\{\begin{array}{l}CH^3\\CH^3\\H\\R\end{array}\right.$

(See SECONDARY ALCOHOLS, p. 215). Our knowledge of the entire trityl-group is very imperfect, and, for the most part, of very recent date.

Of normal trityl-compounds we know common butyric acid, which is



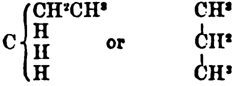
$$C\left\{\begin{array}{l}CH^2CH^3\\H\\H\\COOH\end{array}\right.\quad\text{or}\quad\begin{array}{c}CH^3\\|\\CH^2\\|\\CH^2\\|\\HOCO,\end{array}$$

being "propylated" acetic acid, or, what is the same thing, a compound of normal propyl with oxatyl (O = C-OH)'. (Frankland and Duppa.)

Propylamine, obtained by Mendius, who treated cyanide of ethyl with nascent hydrogen, is a normal trityl-compound, giving, as Chapman and Thorp have shown, propione-aldehyde and propionic acid when subjected to the process of "limited oxidation."

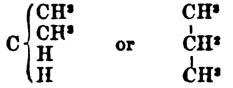
Hydride of propyl must belong to both the normal and the iso-series, as is obvious on inspection of the formulæ:

Normal propylic hydride.



$$C\left\{\begin{array}{l}CH^2CH^3\\H\\H\\H\end{array}\right.\quad\text{or}\quad\begin{array}{c}CH^3\\|\\CH^2\\|\\CH^3\end{array}$$

Isopropylic hydride.



$$C\left\{\begin{array}{l}CH^3\\CH^3\\H\\H\end{array}\right.\quad\text{or}\quad\begin{array}{c}CH^3\\|\\CH^2\\|\\CH^3\end{array}$$

In both normal- and iso-hydride of propyl, there is an atom of carbon which is directly united with two atoms of hydrogen and with two equivalents of carbon belonging to separate atoms of carbon.*

With the exception of butyric acid and its derivatives, propylamine and its derivatives, cyanide of propyl and propyl-hydride, wherein the two series become fused together, there is at the present date (1867) no known compound which can be said with certainty to contain normal propyl. Whether a numerous set of normal propyl-compounds is inherently impossible, or only not discovered, remains to be seen.

One of the earliest (if not the earliest) recognitions of the trityl-group is to be found in Chancel's note in the Comptes Rendus, xxxvii. 410 (1853), which describes a trityl-alcohol extracted by fractional distillation from large quantities of crude amylic alcohol. Great uncertainty surrounds this research of Chancel's, which requires confirmation by the much-improved methods of later years, before we can receive it as an established fact that some varieties of fusel-oil contain tritylic alcohol.

Attempts to form normal trityl-alcohol by synthesis have hitherto failed. Attempts have been made to produce it by means of propylamine, prepared by the method of Mendius from cyanide of ethyl and nascent hydrogen. Nitrous acid attacks the propylamine, but no modification of the method of experimenting has yet succeeded in converting the propylamine into the normal alcohol. The attempt to make it through the aldehyde— which, if Williamson's reaction were of general application, should be formed by the distillation of a mixture of propionate and formate of barium—has miscarried even earlier in the process, for, according to recent researches, propione-aldehyde itself fails to be formed.

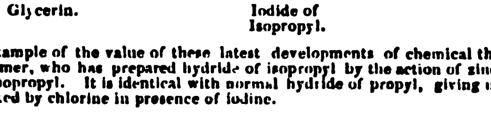
It yet remains to try to add hydrogen to the normal propione-aldehyde obtained by the oxidation of Mendius's propylamine, or to chlorinate the hydride of propyl, and then proceed, through the resulting chlorine-compound, to the acetic ether and alcohol.

Isopropyl-compounds are, on the other hand, obtained with facility, and in a perfectly satisfactory condition.

Berthelot has shown that propylene, the olefine of the group, is easily hydrated by means of acids:

$$\underset{\text{Propylene.}}{C^3H^6} + H^2O = \underset{\text{Isopropyl-alcohol.}}{C^3H^8O.}$$

Erlenmeyer has transformed glycerin into iodide of isopropyl, which is capable of giving the isoalcohol:



$$\left\{\begin{array}{c}H^2COH\\|\\HCOH\\|\\H^2COH\end{array}\right. + 5HI = \begin{array}{c}H^2CH\\|\\HCI\\|\\H^2CH\end{array} + 3H^2O + 2I^2.$$

Glycerin. Iodide of Isopropyl.

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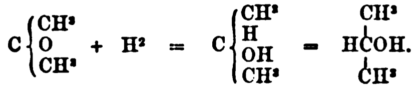
* A striking example of the value of these latest developments of chemical theory has just been given by Schorlemmer, who has prepared hydride of isopropyl by the action of zinc and hydrochloric acid on iodide of isopropyl. It is identical with normal hydride of propyl, giving normal chloride of propyl when attacked by chlorine in presence of iodine.

Finally, Friedel has added hydrogen to acetone, and produced the iso-alcohol. This important reaction completely clears up the structure of the isopropyl-compounds:



$$C\left\{\begin{array}{l}CH^3\\O\\CH^3\end{array}\right. + H^2 = C\left\{\begin{array}{l}CH^3\\H\\OH\\CH^3\end{array}\right. = \begin{array}{c}CH^3\\|\\HCOH.\\|\\CH^3\end{array}$$

Acetone. Isopropyl-alcohol.

(See SECONDARY ALCOHOLS, p. 215.) J. A. W.

TRITYL ALCOHOLS. Normal trityl alcohol is not known with certainty. It is said to boil at 96° to 97°, and to be a fruity liquid, very soluble in water, but not soluble in all proportions, and to be contained in some samples of crude amylic alcohol. (Chancel, Compt. rend. [1853] xxxvii. 410.)

A tritylsulphuric acid, formed by the action of sulphuric acid on the alcohol, is also described.

Isotrityl alcohol, or *Isopropyl alcohol*, or *Pseudopropyl alcohol*, or *Propylene-hydrate.*—Formed, as just described, from propylene, glycerin, or acetone.

Preparation.—α. From Oxalate, or Acetate of Isopropyl, which may be easily decomposed by potash or soda. If the alcohol is wanted in large quantities, this would probably prove the most convenient process, inasmuch as the iodide of isopropyl, from which the oxalate or acetate may be readily prepared, is easily obtained pure and in large quantity.

β. From Acetone.—One vol. of acetone is added to 5 vols. of water, and then treated with sodium-amalgam. After a while, an oily layer separates. The whole liquid is then to be distilled, and the oily distillate mixed with water, and again treated with sodium-amalgam. By repeating this process six times, a transformation of much of the acetone into the isoalcohol is effected. In order to purify the product, it is dried with carbonate of potassium and distilled, then rubbed up with powdered and well-dried chloride of calcium. The mass is subsequently dried in a vacuum over sulphuric acid, when the acetone evaporates, leaving a dry powder, consisting of the compound of isoalcohol with chloride of calcium. Simple heating drives off the isoalcohol from this compound, and rectification suffices to purify it completely. (Linnemann, Ann. Ch. Pharm. cxxxvi. 37.)

Properties.—Isopropyl alcohol is a colourless, not very mobile liquid, having a peculiar odour, not at all resembling that of amyl alcohol. Boils at 83°—84°, under a pressure of 739 mm. At 15°, its specific gravity is 0·791. It does not freeze at −20°. It does not act on polarised light. It is very difficult to dry, mixing with water in all proportions, and forming several hydrates of considerable stability. The existence of these hydrates was first observed by Erlenmeyer, and afterwards confirmed by Linnemann. The following is the composition of these hydrates:

I. ($3C^3H^8O.2H^2O$) boils at 78°—80°; specific gravity, 0·832 at 15°.
II. ($2C^3H^8O.H^2O$) „ 80°
III. ($3C^3H^8O.H^2O$) „ 81°; specific gravity, 0·800 at 15°.

The second, discovered by Erlenmeyer, simulates common alcohol, having exactly the same percentage composition as that substance. It boils only slightly higher than common alcohol, and retains water so strongly, that it does not render blue the white anhydrous sulphate of copper. In order to dehydrate it completely, it is well to use a little metallic sodium. To distinguish between this hydrate and common ethylic alcohol, the readiest plan is to submit the liquid to the action of *iodine* and *phosphorus*, which transforms the one into iodide of isopropyl, and the other into iodide of ethyl. The resemblance extends very far. Both compounds yield acetic acid on *oxidation*, the hydrate of isopropyl alcohol giving, however, carbonic acid in addition.

The characteristic property of isopropyl alcohol is, that it yields acetone by oxidation with dilute chromic acid. This important observation was made by Friedel, after it had been predicted, in a most remarkable manner, by Kolbe, who had had, so to speak, a vision of the secondary alcohols with their leading characteristics. On pushing the oxidation further, the acetone breaks up into acetic acid, carbonic anhydride, and water:

$$C\left\{\begin{array}{l}CH^3\\CH^3\\H\\OH\end{array}\right. + O = C\left\{\begin{array}{l}CH^3\\CH^3\\O\end{array}\right. + H^2O.$$

Isopropyl alcohol. Acetone.

$$C\left\{\begin{array}{l}CH^3\\CH^3\\O\end{array}\right. + O^4 = C\left\{\begin{array}{l}CH^3\\O\\OH\end{array}\right. + CO^2 + H^2O.$$

Acetone. Acetic acid.

Bromine attacks isopropyl alcohol, withdrawing hydrogen, and leaving acetone. In practice, this reaction is very complicated, the hydrobromic acid resulting from this change attacking some of the isoalcohol, and giving bromide of isopropyl, and the acetone suffering a further attack.—Distilled with *acetate of potassium* and *sulphuric acid*, it yields acetate of isopropyl.—Digestion at 140° with *acetic acid* also gives the acetate of isopropyl. The butyric ether is formed similarly, and distils at about 130°.

J. A. W.

TRITYL ETHERS. The normal trityl ethers are scarcely known, but several isotrityl ethers have been prepared:—

Bromide of Isopropyl, C^3H^7Br, is obtained by heating the alcohol with hydrobromic acid, also by the action of bromine on the iodide of isopropyl. It is a liquid. Specific gravity = 1·320 at 13°. Boiling-point = 60° to 63° at 739 mm. pressure.

Chloride of Isopropyl, C^3H^7Cl, prepared by the action of hydrochloric acid on the alcohol, is a liquid, boiling at 36° to 38°, at 741 mm. pressure. Specific gravity at 10° = 0·874.

Cyanide of Trityl, $C^3H^7.CN$. (See BUTYRONITRILE, i. 698.)—This compound is obtained from normal butyric acid, and yields normal butyric acid and ammonia when it is made to take up water.

Cyanide of Isopropyl, C^3H^7CN. (Erlenmeyer.)—When 1 at. iodide of isopropyl and 1 at. cyanide of potassium, dissolved in alcohol, are digested in the water-bath, iodide of potassium is formed, the liquid acquires a very disagreeable smell, and there results an alcoholic solution of cyanide of isopropyl. It is difficult to separate the alcohol from the cyanide, which boils at about 80°. On boiling cyanide of isopropyl with alcoholic potash, ammonia is evolved, and isobutyrate of potassium produced:

$$C^3H^7CN + 2H^2O = C^3H^7COOH + NH^3.$$

Isobutyric acid is quite distinct from butyric acid, and was the first recognised example of an iso-fatty acid.

Iodide of Isopropyl, C^3H^7I. (Erlenmeyer, Zeitschr. Ch. Pharm. 1861, pp. 362, 673.)—Obtained by the action of hydriodic acid on propylglycol, iodide of allyl, isopropyl alcohol, propylene, or glycerin. It is most conveniently prepared by distilling glycerin with a great excess of strong hydriodic acid:

$$C^3H^8O^3 + 5HI = C^3H^7I + 3H^2O + 2I^2.$$

The reaction is perfectly neat, if proper precautions be taken. The conditions to be satisfied are these:—The hydriodic acid used must be sufficiently strong (boiling-point about 125°); if too dilute it may be concentrated by distillation, the strong acid remaining behind in the retort. There must be always great excess of hydriodic acid. The iodine set free should be reconverted into hydriodic acid by means of phosphorus. The operation succeeds either on the small or the large scale. The iodide of isopropyl has been recently manufactured in quantity.

Preparation.—100 lbs. of iodine, 5 lbs. of phosphorus, and 100 lbs. (or rather more) water, are employed. A little of the water is warmed, and put into a large vessel; and the iodine and phosphorus and water are added by degrees, and well stirred up. The stirring renders the reaction quite manageable. The first quantity of water is warmed to start the reaction, afterwards the water is added cold. In this way there is obtained a strong solution of hydriodic acid containing also some phosphoric acid. This solution is put into an iron still and distilled, until very concentrated hydriodic acid begins to pass over. When the concentration is sufficient, a charge of 11 lbs. of glycerin is put into the still, and 3 lbs. of phosphorus added by degrees. A very energetic action is thus set up, and iodide of isopropyl distils over very rapidly, accompanied by water and hydriodic acid. When the action has become moderate, a second charge of 11 lbs. of glycerin and 3 lbs. of phosphorus is introduced into the still. When the second charge has worked off, a small third charge may be put in.

Ultimately the products are iodide of isopropyl, hydriodic acid, and phosphoric acid. When the phosphoric acid has accumulated, it is necessary to distil off. The hydriodic acid is ready for a second operation. By operating as above described, a quantity of iodide of isopropyl may be obtained, very close upon that required by theory, and in a series of operations very nearly all the iodine used may be transformed into the organic iodide.

The iodine, as it is set free, is transformed into hydriodic acid by the action of the phosphorus and water, and becomes available.

If an insufficient quantity of hydriodic acid be allowed to act on the glycerin in the above process, the iodide of isopropyl will be contaminated with iodide of allyl.

Maxwell Simpson has shown that iodide of allyl is transformed into iodide of isopropyl by treatment with hydriodic acid.

Properties.—Iodide of isopropyl is an oil, boiling at 89° to 90°, under a pressure of 735 mm. Specific gravity 1·70 at 15°. In smell it resembles iodide of ethyl. It is nearly insoluble in water, and dissolves phosphorus and iodine.

With *sodium*, in presence of ether, it gives propylene, hydride of propyl, and di-isopropyl (Schorlemmer).—*Bromine* drives out the iodine, forming a bromide of the radicle.—*Chlorine* attacks it more deeply, giving, among other products, trichlorhydrin, $C^3H^5Cl^3$.—With *oxalate of silver*, it gives oxalate of isopropyl.—With *acetate of silver*, it yields acetate of isopropyl, boiling at 90°—93°, according to Friedel.

With *oxide of silver* and *water*, it gives isopropyl ether, $\left.\begin{matrix} C^3H^7 \\ C^3H^7 \end{matrix}\right\} O$, isopropyl alcohol, and propylene, C^3H^6.

With *alcoholic potash* it gives propylene. It reacts on *ammonia*, giving some propylene and an organic base. It forms new bases when made to act on *aniline* or on *rosaniline*.

Carefully oxidised with dilute *chromic acid*, it gives acetic and carbonic acids, and no propionic acid. (Chapman and Thorp.) J. A. W.

TRITYL, HYDRIDE OF. This compound appears to occur in American petroleum (Ronalds). By heating to 275° a mixture of bromide of propylene, $C^3H^6Br^2$, iodide of potassium, and water, with metallic copper, there is obtained propylene, hydride of propyl, and carbonic acid. Hydride of propyl is a gas, which is soluble in alcohol. J. A. W.

TRITYLAMINE, or **PROPYLAMINE.** $N\left\{\begin{matrix} C^3H^7 \\ H \\ H \end{matrix}\right.$.—This base is isomeric with trimethylamine, which has often been mistaken for it. The only process by which it has been prepared is that of Mendius, viz., by the hydrogenation of cyanide of ethyl:

$$C^2H^5CN + H^4 = C^3H^9N.$$

To prepare propylamine, 36 grms. of cyanide of ethyl, 500 grms. of common alcohol, 200 grms. of water, and 500 grms. of 20 per cent. hydrochloric acid, are allowed to act on excess of granulated zinc, and then distilled. The distillate is put back once, and 400 grms. of hydrochloric acid are added. The product is distilled to get rid of the alcohol, then excess of alkali added to the residue, and the distillation continued, whereupon propylamine and water come over.

From 36 grms. of the cyanide of ethyl, 9 grms. of pure propylamine have been obtained (Mendius). Propylamine is dried by distillation from solid potash.

Properties.—Bright, colourless, highly refracting, very mobile liquid, possessing a peculiar, strongly ammoniacal odour, very different from that of methylamine. It is miscible with water, becoming hot in contact with it. Boils at 50°. Its aqueous solution precipitates the oxides of iron, copper, lead, aluminium, nickel, cobalt, and mercury, and does not dissolve the precipitate when added in excess.

The precipitate formed with silver-solutions is soluble in excess.

The propylamine, prepared as just described, is a true normal propyl-compound, giving, on oxidation with dilute chromic acid, propione-aldehyde and propionic acid, and not giving any carbonic acid or acetic acid. (Chapman and Thorp.)

It combines with acids, forming crystallisable salts.—The *chloride*, NC^3H^9HCl, forms very deliquescent crystals, freely soluble in alcohol, almost insoluble in ether. A little above 100° it melts, and sublimes unchanged. It may be obtained, in large square plates, by crystallisation from strong alcohol.—The *chloroplatinate*, $2NC^3H^{10}Cl.PtCl^4$, is moderately soluble in hot water and alcohol, and insoluble in ether. It often forms fine crystals, a quarter of an inch long.

Sulphate of propylamine is crystalline and deliquescent.

On treating propylamine with *iodide of ethyl*, the following products are obtained:

$$\begin{matrix} N\left\{\begin{matrix} C^3H^7 \\ C^2H^5 \\ H \end{matrix}\right. & \qquad N\left\{\begin{matrix} C^3H^7 \\ C^2H^5 \\ C^2H^5 \end{matrix}\right. & \qquad N\left\{\begin{matrix} C^3H^7 \\ C^2H^5 \\ C^2H^5 \end{matrix}\right. . \\ HI & \qquad HI & \qquad C^2H^5I. \end{matrix}$$

The last compound, *iodide of triethyl-propylammonium*, is a white crystalline mass, insoluble in potash-ley. From its alcoholic solution it crystallises in long needles.

Oxide of silver reacts upon it, giving a strongly caustic solution of hydrate of the ammonium-base.—The *chloroplatinate*, $2NC^3H^7(C^2H^5)^3Cl.PtCl^4$, forms deep orange-coloured octahedrons, rather soluble in alcohol and water. (Mendius, Ann. Ch. Pharm. cxxi. 129.) J. A. W.

TRITYLENE, or **PROPYLENE,** C^3H^6, the olefine of the trityl-group, was discovered by Reynolds in 1851. It is obtained, more or less impure, when fusel-oil or valerianic acid is passed through a red-hot tube; by the destructive distillation of oleic acid with lime or soda-lime; and by the destructive distillation of sugar mixed with an equal weight of soda-lime. According to Dusart (Ann. Ch. Pharm. xcvii. 127), it is obtained on distilling an intimate mixture of equivalent quantities of oxalate of calcium and acetate of potassium.

It is prepared most conveniently by acting on iodide of allyl with mercury and strong hydrochloric acid. The mercury should contain a trace of zinc, according to the observation of von Than. The following are the details of the process:—

Iodide of phosphorus is prepared by acting on 1 pt. of phosphorus with 8 pts. of iodine. 50 grms. of this iodide of phosphorus, and 50 grms. of glycerin, distilled together, yield 30 grms. of iodide of allyl. From this quantity of the iodide, 3 litres of propylene may be obtained by employing 150 grms. of mercury and 50 grms. of fuming hydrochloric acid. The gas obtained in this operation is chemically pure propylene. (Berthelot and De Luca, Ann. Ch. Pharm. xcii. 306.)

According to Rieth and Beilstein, chloride of carbon, acted upon by zinc-ethyl, yields a mixture of propylene, ethylene, and chloride of ethyl, also chloride of zinc. Iodide of isopropyl and alcoholic potash also give propylene.

Properties.—Colourless gas, not condensable at – 140°. It has a distinct phosphoric odour, as is generally the case with the olefines, and a sweetish taste. According to von Than:

100 vols. of water	absorb	44	vols. of propylene	at	0°.
"	"	35	"	"	5°.
"	"	28	"	"	10°.
"	"	23	"	"	15°.
"	"	22	"	"	20°.

Absolute alcohol dissolves 12 to 15 times its volume of this gas—glacial acetic acid 6 volumes.

Like ethylene, it combines readily with *chlorine* and *bromine*, and is capable of uniting with *iodine*; the resulting compounds are $C^3H^6Cl^2$, $C^3H^6Br^2$, $C^3H^6I^2$.

It is absorbed by *cuprous chloride*, but not to the same extent as ethylene.—*Fuming sulphuric acid* absorbs it very readily.—Common *oil of vitriol*, *hydrochloric*, *hydrobromic*, and *hydriodic acids* combine with it far more readily than with ethylene. These acids convert it into isopropyl-compounds.—On oxidation with dilute *chromic acid*, it gives acetic and carbonic acids. It is not very readily oxidised.—With *permanganate of potassium* in an acid liquid, it gives the same products as with chromic acid; with permanganate in an alkaline liquid, acetic and formic acids. J. A. W.

TRITYLENIC ALCOHOL. $C^3H^8O^2 = \left.\begin{matrix}(C^3H^6)''\\H^2\end{matrix}\right\}O^2$. *Trityl, or Propylglycol.* —Prepared from the tritylenic acetate just described, by distillation with caustic potash, in the oil-bath. It is a colourless oily liquid, sweet to the taste, soluble in water and alcohol in all proportions, and soluble in 12 to 13 pts. of ether. Its specific gravity at 0° is 1·051. Boiling-point 188° to 189°.

Platinum-black oxidises it to lactic acid:

$$\underset{\text{Tritylenic hydrate.}}{C^3H^8O^2 + O^2} = \underset{\text{Lactic acid.}}{C^3H^6O^3} + H^2O.$$

Digested at 100° for some hours with strong *hydriodic acid*, it gives iodide of isopropyl (Wurtz):

$$C^3H^8O^2 + 3HI = C^3H^7I + 2H^2O + I^2.$$

With *pentachloride of phosphorus* it gives chloride of propylene, $C^3H^6Cl^2$.

Heated with dilute *nitric acid*, it is broken up into glycollic acid, whilst concentrated nitric acid resolves it into oxalic acid. J. A. W.

TRITYLENIC ETHERS. The *acetate*, $C^7H^{12}O^4 = \left.\begin{matrix}C^3H^6\\(C^2H^3O)^2\end{matrix}\right\}O^2$, was discovered by Wurtz. 320 grms. acetate of silver, 192 grms. bromide of propylene, and sufficient glacial acetic acid to bring the mixture into a semifluid state, are heated in the water-bath for four days, then mixed with ether and filtered, and the filtrate is distilled. The acetate is a colourless neutral liquid, soluble in 10 pts. of water, and boiling at 186°. Its specific gravity at 0° = 1·109.

The *bromide*, $C^3H^6Br^2$, formed directly from propylene and bromine, is a colourless oily liquid. Specific gravity = 1·974. Boiling-point 144°. It is a convenient compound for the preparation of proplylene-derivatives.

The *chloride*, $C^3H^6Cl^2$, is a liquid boiling at 103°. Specific gravity = 1·151.

The *cyanide*, $C^3H^6(CN)^2$, was discovered by Maxwell Simpson. 1 at. tritylenic bromide and 2 at. cyanide of potassium are heated with a large quantity of alcohol to 100° for about 16 hours. The product is then filtered, and deprived of alcohol by evaporation. The residue is treated with ether, and the ethereal solution evaporated to get rid of the ether, and then distilled. In this way tritylenic cyanide is obtained as a liquid, boiling between 277° and 290°. It is soluble in water, alcohol, and ether.

Heated with 1½ vols. of strong *hydrochloric acid* to 100°, it suffers a very interesting change, yielding pyrotartaric acid. In order to extract this acid, the residue, after the reaction, is treated with absolute alcohol, which dissolves the acid; the alcoholic solution is evaporated. to drive off the alcohol; and the residue crystallised from aqueous solution, and finally dissolved in ether, which on evaporation leaves the pyrotartaric acid in a state of purity:

$$\underset{\substack{\text{Cyanide of}\\\text{propylene.}}}{C^3H^6(NC)^2} + 4H^2O = \underset{\substack{\text{Pyrotartaric}\\\text{acid.}}}{C^5H^8O^4} + 2NH^3.$$

The *iodide*, $C^3H^6I^2$, is a liquid which does not solidify at −10°. It was discovered by Berthelot and De Luca (Ann. Ch. Pharm. xcii. 311). Prepared by exposing iodine in contact with propylene to sunlight, or by heating it to 50° or 60°. The resulting liquid is freed from excess of iodine by treatment with potash. It is decomposed by alcoholic potash into propylene and other products.

The *sulphide*, $C^3H^6S^2$, is a white amorphous powder, obtained by the action of tritylenic bromide on an alcoholic solution of sulphide of sodium.

The *sulphocarbonate*, $C^3H^6CS^3$, is easily obtained from an alcoholic solution of sulphocarbonate of sodium and tritylenic bromide. It is a thick liquid of disagreeable smell, and of a yellowish-brown colour. Specific gravity = 1·31 at 20°. It may be distilled in a stream of hydrogen. J. A. W.

TRITYLPHYCITE or **PROPYLPHYCITE.** $C^3H^8O^4 = \left.\begin{matrix}(C^3H^4)^{iv}\\H^4\end{matrix}\right\}O^4 = (C^3H^4)^{iv}(HO^4)$. *Glycerylenic Alcohol.*—A tetratomic alcohol, homologous, at least in composition, with phycite or erythromannite, $C^4H^{10}O^4$ (ii. 504; iv. 633). The corresponding dichlorhydrin, $(C^3H^4)Cl^2(HO)^2$, is produced by addition of hypochlorous acid to ordinary glyceric epichlorhydrin (i. 894):

$$(C^3H^5)'''\left\{\begin{matrix}Cl\\O\end{matrix}\right. + ClHO = (C^3H^4)^{iv}\left\{\begin{matrix}Cl^2\\(HO)^2\end{matrix}\right.;$$

and from this compound, the alcohol is obtained by the action of aqueous alkalis:

$$(C^3H^4)Cl^2(HO)^2 + 2KHO = (C^3H^4)^{iv}(HO)^4 + 2KCl.$$

To prepare propylphycite, the dichlorhydrin just mentioned, or the corresponding dichlorobromhydrin (p. 894), dissolved in 3 vols. alcohol, is mixed with 10 vols. water, and gradually with an excess of finely-divided hydrate of barium suspended in water, the liquid being ultimately warmed till it becomes inodorous. The baryta is then carefully precipitated with sulphuric acid; the filtrate is exactly neutralised with carbonate of lead; the dissolved lead removed by sulphydric acid; the chlorine by careful addition of silver-carbonate; any silver still remaining dissolved by sulphydric acid; and the solution, which is generally colourless (if not, it must be decolorised with animal charcoal), is evaporated over the water-bath. The residue, after being redissolved and evaporated, consists of pure propylphycite. If, however, the dichlorhydrin used in the preparation is not free from ordinary glyceric dichlorhydrin, the product will be contaminated with glycerin. In this case, the solution, freed from barium and chlorine, must be precipitated with basic lead-acetate not added in excess, and the washed precipitate, $C^3H^4.H^2Pb''O^4$, decomposed by sulphydric acid.

Propylphycite is a colourless, solid, amorphous mass,* which, on exposure to the air, quickly deliquesces to a glutinous liquid. It has a sweetish taste, is easily soluble in alcohol, does not decompose at 150°, and, if carefully heated, volatilises with only partial decomposition. In its chemical relations it resembles phycite, $C^4H^{10}O^4$. Like the sugars, it is very easily altered by acids, alkalis, and oxidising agents. On evaporating it with dilute acids or bases, it turns brown, and a humus-like body is separated.

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* In removing the chlorine with silver-chloride, or the chlorine and barium by silver-sulphate, a crystalline substance was obtained, nearly related to propylphycite, and perhaps containing $C^3H^6O^4$. (Carius.)

With cupric oxide and potash, it forms a blue solution, which does not deposit cuprous oxide on boiling, even if the propylphycite has previously been treated with dilute sulphuric acid. From a neutral silver-solution, it reduces the metal at the boiling heat; from an ammoniacal solution, even at ordinary temperatures.

Propylphycite contains four atoms of hydrogen replaceable by metals or other radicles, two of them apparently with greater facility than the other two. In concentrated solution it takes up lime, baryta, lead-oxide, and even lead- or silver-carbonate. The solution containing lime, baryta, or lead-oxide yields, with alcohol, white bulky precipitates, soluble in water, and decomposible by carbonic acid. The lead-compound, in aqueous solution, is not completely decomposed by sulphydric acid, the filtrate still giving a precipitate with sulphide of ammonium. The compound formed on adding basic acetate of lead to a solution of propylphycite, is a bulky precipitate, soon becoming granular, and containing $C^3H^4.H^2Pb''O^4$.

Nitropropylphycite, $C^3H^4.H^2(NO^2)O^4$, is formed by dropping a scarcely liquid solution of propylphycite into cooled fuming nitric acid, and separates, on pouring the liquid into water, as a colourless viscid mass, nearly insoluble in water, but soluble in alcohol and ether. The nitro-compound becomes mobile at 100°, distils for the most part without decomposition, if carefully heated, but when quickly heated, decomposes suddenly, though without explosion. Zinc and hydrochloric acid, added to its alcoholic solution, produce chloride of ammonium and propylphycite.

TRITYLPHYCITIC or **PROPYLPHYCITIC ACID.** $C^3H^6O^5 = \left.\begin{matrix}(C^3H^2O)^{iv}\\ H^4\end{matrix}\right\}O^4$. (Carius, *loc. cit.*)—Produced by dissolving propylphycite in nitric acid of specific gravity 1·2, diluted with an equal volume of water, repeatedly evaporating the solution, neutralising with carbonate of barium, filtering from oxalate of barium, and precipitating the concentrated filtrate with alcohol. The acid, separated from the barium-salt by sulphuric acid, is a colourless, amorphous, strongly acid, deliquescent mass, which decomposes at 160°, either in the free state or combined with bases, yielding oxalic, acetic, and perhaps also glycollic acid.

The propylphycitates, excepting the lead- and silver-salts, are easily soluble; the *silver-salt* is very quickly reduced in ammoniacal solution.—The *acid barium-salt*, $C^6H^{10}Ba''O^{10} = C^3H^4Ba''O^5.C^3H^6O^5$, is an indistinctly crystalline powder.—The *acid calcium-salt*, $C^6H^{10}Ca''O^{10} = C^3H^4Ca''.O^5.C^3H^6O^5$, is not crystallisable, but is precipitated by alcohol from its aqueous solution in flocks.—The *acid lead-salt*, $C^6H^{10}Pb''O = C^3H^4Pb''O^5.C^3H^6O^5$, precipitated by neutral lead-acetate, is flocculent at first, but afterwards changes to a crystalline powder, composed of microscopic prisms.—The *normal lead-salt*, $C^3H^2Pb^2O^4$, precipitated by basic lead-acetate, is an amorphous powder.

TRITYLPHYCITIC or **PROPYLPHYCITIC DICHLORHYDRIN.** $C^3H^6Cl^2O^2 = C^3H^4.Cl^2(HO^2)$. *Glycerylenic Dichlorhydroxylate.* (Carius, *loc. cit.*)—This compound is formed, as already stated (p. 893), by addition of hypochlorous acid to glyceric epichlorhydrin.

To prepare it, epichlorhydrin is added in the dark, and with frequent agitation, to a cooled solution of hypochlorous acid (prepared by passing chlorine-gas into water in which mercuric oxide is suspended, and containing from 6 to 8 per cent. of the acid), till the odour becomes barely perceptible; the solution, filtered from mercuric oxychloride and diluted, is immediately treated with sulphydric acid gas, till the excess of hypochlorous acid is decomposed and the mercury is precipitated; the filtrate is then saturated with common salt; and the dichlorhydrin, already partly separated as an oily liquid, is further extracted by agitation with ether, and purified, after evaporation of the ether, by heating it to 160°—170° in a stream of dry carbonic anhydride, whereby any glyceric dichlorhydrin formed at the same time is decomposed.

Propylphycitic dichlorhydrin, thus obtained, is a liquid, rather mobile when warm, but of the consistence of glycerin at ordinary temperatures; it is heavier than water, has a somewhat rancid odour, dissolves easily in alcohol and in ether, but is nearly insoluble in salt-water. When heated above 200°, it decomposes, giving off hydrochloric acid, and vapours smelling of acrolein. By potash in aqueous solution, it is easily converted into propylphycite:

$$C^3H^4\left\{\begin{matrix}Cl^2\\ (HO)^2\end{matrix}\right. + 2KHO = \left.\begin{matrix}C^3H^4\\ H^4\end{matrix}\right\}O^4 + 2KCl.$$

TRITYLPHYCITIC or **PROPYLPHYCITIC DICHLOROBROMHYDRIN**, $C^3H^4\left\{\begin{matrix}Cl^2Br\\ HO\end{matrix}\right.$, is produced by heating 1 at. of the dichlorhydrin to 120°, in sealed tubes, with 1 at. dry bromine. It is a mobile liquid, having a sharp odour, decomposing at 160°, insoluble in water, but decomposed by it, with separation of bromine and hydrochloric acid. With alkalis, it reacts like the dichlorhydrin. (Carius.)

TRITYLPHYCITIC or **PROPYLPHYCITIC ETHERS.** (Carius, *loc. cit.*) —*Diaceto-propylphycite*, $C^3H^4.H^2(C^2H^3O)^2O^4$, is obtained by heating the dichlorhydrin to 100° with sodic acetate and glacial acetic acid, neutralising with sodic carbonate, and exhausting with ether. It is a viscid bitter liquid, easily soluble in water, not capable of being distilled without decomposition. Baryta decomposes it into acetic acid and propylphycite.

Triethylpropylphycite, $C^3H^4.H(C^2H^5)^3O^4$, is produced by gradually mixing an alcoholic solution of the dichlorobromhydrin with diluted and cooled sodium-ethylate, or by heating it to 150° with absolute alcohol. It is a colourless, faintly smelling lipuid, easily soluble in water and in potash-ley, heavier than water, and dissolving calcium-chloride in considerable quantity. Boiling-point = 192·8° at 0·758 met. Vapour-density, obs. = 6·65; calc. = 6·79.

Tetrethylpropylphycite, $C^3H^4(C^2H^5)^4O^4$, is produced, as shown by the equation:

$$\left.\begin{matrix}C^3H^4\\(C^2H^5)^3Na\end{matrix}\right\}O^4 + C^2H^5I = NaI + \left.\begin{matrix}C^3H^4\\(C^2H^5)^4\end{matrix}\right\}O^4,$$

by warming the triethylic ether with sodium as long as hydrogen is thereby evolved, and distilling the resulting sodium-compound with an equivalent quantity of ethylic iodide. It is a rather mobile colourless liquid, which boils between 150° and 160°, and exhibits, more plainly than the preceding compound, the odour of sugar heated above its melting-point.

Diaceto-diethylpropylphycite, $C^3H^4(C^2H^3O)^2(C^2H^5)^2O^4$, is formed, together with ethylic acetate, by heating triethylpropylphycite to 150° for several hours, with 3 vols. glacial acetic acid. It is a thick colourless liquid, which boils at about 210°, and is decomposed by baryta-water into barium-acetate, and a liquid compound soluble in water, probably consisting of diethylpropylphycite.

TROMBOLITE. Syn. with THROMBOLITE (p. 788).

TRONA. Native tetrasodic carbonate, or sesquicarbonate, $2Na^2O.H^2O.3CO^2.2aq.$ (See CARBONATES, i. 796.)

TROOSTITE. A silicate of manganese and zinc, from Sterling, in New Jersey (p. 254).

TROPÆOLIC ACID. See the next article.

TROPÆOLUM. The common nasturtium, *Tropæolum majus*, contains in 100 pts., besides the ordinary plant-constituents, 2·1 pts. volatile oil, 8·6 lime, 2·3 silica, and 0·9 of a peculiar acid called tropæolic acid. The volatile oil and the tropæolic acid are found in the entire plant, especially in the fruit and seed-coatings. The volatile oil has a peculiar odour, a sharp burning taste, and reddens the skin.

Tropæolic acid is extracted from the herb or the seed with alcohol; and on boiling the solution with water, and evaporating the filtrate, the acid crystallises in slender needles. It is white, reddens litmus strongly, and forms crystallisable salts with potash and soda (Müller, Ann. Ch. Pharm. xxv. 208). Whether this body is really a peculiar acid, further investigation must decide. According to experiments by v. Payr, communicated by Rochleder (Jahresb. 1857, p. 522), the crystals obtained by Müller were nothing but sulphate of potassium, which, however, does not agree with Müller's statement that they were soluble in alcohol and ether.

The seeds and flower-buds of *Tr. majus* pickled with vinegar are sometimes used instead of capers.

TROPINE. $C^8H^{15}NO$. (Kraut, Ann. Ch. Pharm. cxxviii. 280; cxxxiii. 87; Jahresb. 1863, p. 448; 1865, p. 448.)—An organic base, produced, together with atropic acid,* by the decomposition of atropine with alkalis:

$$\underset{\text{Atropine.}}{C^{17}H^{23}NO^3} = \underset{\text{Atropic acid.}}{C^9H^8O^2} + \underset{\text{Tropine.}}{C^8H^{15}NO.}$$

Atropine, heated with hot saturated baryta-water, disappears almost entirely, while only traces of a volatile base are produced. On precipitating the baryta from the resulting solution by carbonic acid, atropate of tropine remains in solution; and on agitating the filtered liquid with hydrochloric acid and ether, the atropic acid is dissolved by the ether, while hydrochlorate of tropine remains in the watery liquid. The base separated from this salt by silver-oxide solidifies in the crystalline form over oil of vitriol, and, when distilled at a temperature above 230°, passes over as a turpentine-like mass, and ultimately forms crystals containing $C^8H^{15}NO.\frac{1}{2}H^2O$.

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* The name "atropic acid" has also been given to an imperfectly known acid, said by Richter to exist in belladonna (i. 474).

Atropine is likewise resolved into atropic acid and tropine, by the action of fuming hydrochloric acid.

Tropine is inodorous in the cold, but gives off odorous vapours when heated. It has a strong alkaline reaction, dissolves easily in water and in alcohol, and remains as an oil on evaporation. From solution in anhydrous ether, it crystallises over oil of vitriol in colourless anhydrous tables, $C^8H^{15}NO$, which melt at 61·2°. It does not absorb carbonic acid from the air, forms salts which crystallise well, and its aqueous solution precipitates the oxides of silver and copper, the precipitates not being soluble in excess of the reagent. From the solution of hydrochlorate of tropine, $C^8H^{15}NO.HCl$, strong potash-ley throws down oily drops, soluble in ether and in water.

The *chloroplatinate*, $2(C^8H^{15}NO.HCl).PtCl^4$, forms large orange-red crystals, easily soluble in water, but insoluble in alcohol. The double salts formed by the hydrochlorate with mercuric chloride, and by the hydriodate with mercuric iodide, are also sparingly soluble, and easily crystallisable. Auric chloride forms, in the solution of the hydrochlorate, a yellow precipitate, which melts and dissolves in warm water, and then crystallises.—*Picrate of tropine*, $C^8H^{15}NO.C^6H^3(NO^2)^3O$, is a yellow precipitate, which crystallises from water in needles.—*Atropate of tropine*, $C^8H^{15}NO^2.C^9H^8O^2.4H^2O$, is uncrystallisable, nearly solid, and ropy at ordinary temperatures, deliquescent at higher temperatures. In a 2 per cent. aqueous solution it does not produce dilatation of the pupil.

Tropine is not decomposed by boiling with hydriodic acid, or by heating to 140°, with hydrochloric acid. When distilled with dry hydrate of barium, it gives off ammonia and methylamine, together with other products.

Hydriodate of Ethyltropine, $C^8H^{14}(C^2H^5)NO.HI$, is easily formed by dissolving tropine in ethylic iodide. The free base separated from it by silver-oxide is a brown amorphous mass, which is insoluble in ether, soluble in absolute alcohol, and does not take up another atom of ethyl when treated with ethylic iodide.—The *platinum-salt*, $2[C^8H^{14}(C^2H^5)NO.HCl].PtCl^4$, is a light-yellow crystalline powder, precipitable by alcohol.

TRUFFLE. *Tuber cibarium* (*Lycopodon tuber*, L.).—An edible fungus, belonging to the family of the Gasteromycetes, forming round, blackish, warty knobs, yellowish-white within, veined like nutmegs, having a peculiar, agreeable, musklike odour, and aromatic taste. Truffles grow underground, often in groups: they occur in all temperate climates, especially in oak, beech, and chestnut-woods, and thrive best in a calcareous marly soil.

The aroma of the truffle is very volatile, and passes over with water in distillation. According to Lefort, truffles, when perfectly ripe, contain about 70 per cent. water. The organic constituents of the truffle are mannite, malic acid, citric acid, a non-saponifiable fat, besides the ordinary constituents of vegetable substances. Glucose, which (according to Vauquelin, Braconnot, and Lefort) occurs in *Agaricus edulis*, is not found in truffles (according to Lefort). The peculiar odoriferous principle of the truffle does not belong to the class of volatile oils: the colouring-matter exists chiefly in the spores.

TSCHEFFKINITE or **TSCHEWKINITE.** A silicotitanate of iron, cerium, &c., occurring massive and apparently amorphous, near Miask in the Ilmen Mountains. It is nearly opaque, with velvet-black colour, dark-brown streak, and strong vitreous lustre. Hardness = 5·0 to 5·5. Specific gravity = 4·50 to 4·55. Fracture flat conchoïdal. When heated before the blowpipe, it quickly glows, swells up very strongly, turns brown, and melts to a black bead. With fluxes it gives the reactions of iron, manganese, and silica. When heated in a tube, it leaves a little water. It dissolves in hydrochloric acid, leaving a jelly of silica. It contains, according to an approximate analysis by H. Rose (Pogg. Ann. lxii. 591):

SiO^2.	TiO^2.	CeO; LaO; DiO.	FeO.	CaO.	MgO.	MnO.	K^2O; Na O.
21·04	20·17	47·29	11·21	3·50	0·22	0·83	0·12;

whence its composition appears to be expressible by the formula $M''SiO^3.M''TiO^3$. A mineral from Coromandel, analysed by Damour (Jahresb. 1861, p. 824) appears to have the same composition. Another mineral, analysed by Schubin (Berz. Jahresb. xxvi. 373), and designated as tschewkinite, has been shown by Kokscharow to consist of orthite.

TSCHEN. Chinese coins of brass-yellow to bronze-yellow colour, containing (in 100 pts.) 55 to 64 per cent. copper, 26 to 35 zinc, generally from 1 to 2 per cent. tin. 2 to 4 per cent. iron, and between 1 and 6 per cent. lead; some of them contain also small quantities of antimony, arsenic, and nickel. (Pöpplein, Chem. Centr. 1859, p. 484.)

TSCHERMIGITE. Ammonia-alum (p. 580), occurring in a bed of lignite at Tschermig in Bohemia; also, according to Peters (Leonh. Jahresb. f. Min. 1861, p. 566), in that of Tokod, near Gran in Hungary.

TSCHEWKINITE. Syn. with TSCHEFFKINITE.

TSCHORNOSEM. Russian black earth. (See SOILS, p. 344.)

TSE-HONG. A mixture of white lead with alumina, ferric oxide, and silica, used by the Chinese as a red colour for painting on porcelain. (Salvétat.)

TSING-LIEN is another red colour, used for porcelain-painting, consisting chiefly of stannic and plumbic silicates, together with small quantities of oxide of copper, or cobalt and metallic gold. (Salvétat.)

TUBER CIBARIUM. Syn. with TRUFFLE.

TUESITE. A mineral allied to lithomarge or kaolin, occurring on the banks of the Tweed. It is massive, compact, with a bluish-white colour, and slightly waxy to dull lustre; opaque; sectile. Hardness = 2·5. Specific gravity = 2·4 to 2·6. Before the blowpipe it becomes light-blue and brittle, and forms a colourless glass with borax. The following analyses are by Thompson and Richardson (*Thomson's Outlines of Mineralogy*, i. 244):

SiO^2.	Al^2O^3.	CaO.	MgO.	FeO.	H^2O.		
44·30	40·40	0·75	0·50	. .	13·50	=	99·45.
43·80	40·10	0·64	0·55	0·94	14·21	=	100·24.

TUFA, CALCAREOUS. This name is applied to agaric mineral, or rock-milk (iii. 697), when so hard as not to be friable.

TUFA, VOLCANIC. Earthy or compact masses with white fracture, consisting of the hardened mud formed by mixture of volcanic ash (i. 420) with water.

TULIP-TREE. *Liriodendron tulipifera.*—The root-bark of this tree is said by Emmet to contain a crystallisable bitter principle called liriodendrin (iii. 726), which, however, Bouchardat was unable to prepare. The latter, however, obtained from tulip-tree bark a crystalline body, which he called piperin.

TULUCUNA, TULICOONA, or **TALLICOONA OIL.** Syn. with CARAPA-OIL (i. 749).

TULUCUNIN. $C^{20}H^{14}O^4$.—A crystallisable bitter principle, contained, according to Caventou (J. Pharm. [3], xxxv. 189; Jahresb. 1859, p. 583), in the bark of *Carapa Tulucuna.* Is is prepared by exhausting the aqueous extract of the bark with alcohol, mixing the solution with milk of lime, evaporating it after the insoluble matter has settled down, and treating the residue with chloroform. The resulting solution, when left to evaporate, yields tulucunin as a light-yellow, amorphous, resinous mass, having a very bitter taste, slightly soluble in water, easily soluble in alcohol and in chloroform, insoluble in ether. It is turned blue by sulphuric acid in the cold, and by oxalic, tartaric, or citric acid when heated.

TUNGSTATES. See p. 904.

TUNGSTEN: also called Wolfram. *Atomic weight*, 184. *Symbol*, W.—A metallic element, occurring as tungstate of iron and manganese in wolfram, a mineral somewhat abundant in Cornwall, Saxony, Bohemia, and other localities: it occurs also as tungstate of calcium (scheelite or tungsten) in Bohemia, Saxony, and other places; and as tungstate of lead (scheeletine) at Zinnwald in Bohemia, Bleiberg in Carinthia, and in Chile.

Metallic tungsten is obtained: 1. By heating trioxide of tungsten (tungstic oxide or anhydride) to bright redness in a stream of hydrogen.—2. By mixing the trioxide to a stiff paste with oil, charring the mixture, and then heating it intensely for several hours in a crucible lined with charcoal.—3. By passing the vapour of tungstic chloride or oxychloride mixed with hydrogen through a red-hot glass tube. (Wöhler, Ann. Ch. Pharm. xciv. 255.)

4. By passing the vapour of tungstic chloride over strongly heated sodium, and washing out the resulting sodium-chloride with water. (A. Riche, Ann. Ch. Phys. [3], l. 5.)

5. By igniting nitride of tungsten in hydrogen-gas, or in a porcelain crucible surrounded with charcoal-powder. (Wöhler, Jahresb. 1850, p. 303.)

Tungsten obtained by the first process is described by Wöhler as a steel-grey powder, which melts into globules at a very intense heat. According to Riche, the metal obtained as above forms small crystalline grains, which acquire metallic lustre by burnishing, and scratch glass with facility; it is infusible in the strongest forge-fire, but may be melted by the current of a Bunsen's battery of 200 pairs, being partially oxidised at the same time, and burning with a blue flame. The metal obtained by the second process is also heavy, of iron-grey colour, very hard, and difficult of fusion. The third process yields the metal as a shining, dark steel-grey, specular deposit, which may be detached from the glass in hard brittle crusts.

The specific gravity of tungsten reduced by hydrogen is 17·2 to 17·6 (**Wöhler**); 17·9 to 18·2 (Bernoulli, Jahresb. 1860, p. 152); that of the metal reduced by charcoal is 17·1 to 17·2 (Bernoulli); of that reduced from the chloride by hydrogen, 16·54. (Wöhler.)

Tungsten reduced from the nitride (4) is pulverulent, and has a specific gravity of 17·5; that obtained by igniting acid potassium-tungstate in hydrogen, has a specific gravity of 18·26. (Wöhler.)

Pulverulent tungsten heated in the air, burns easily to tungstic oxide; but compact tungsten may be heated in the air without sensible change, excepting at the very high temperature of the electric current, as above mentioned. Nitric acid and nitromuriatic acid convert tungsten into tungstic acid, and the same change is produced by heating it in contact with the alkalis or with nitre. Pulverulent tungsten is also oxidised and dissolved, by boiling it in a solution of caustic alkalis or alkaline carbonates.

Tungsten forms two classes of compounds, in one of which it is tetratomic, and in the other hexatomic:

Tungstous Chloride, WCl^4.	Tungstic Chloride. WCl^6.
Tungstous Oxide, WO^2.	Tungstic Oxide, WO^3.

There are also compounds of intermediate composition, which may be regarded as resulting from the union of tungstous and tungstic compounds: *e.g.*, $W^2Cl^{10} = WCl^4.WCl^6$.

TUNGSTEN, ALLOYS OF. These alloys have not been much studied. Wöhler and Michel (Ann. Ch. Pharm. cxv. 102), by fusing 15 pts. tungsten-trioxide, 30 pts. cryolite, 30 pts. of a mixture of potassium- and sodium-chloride in equivalent proportions, and 15 pts. aluminium at a full red heat, obtained a regulus, which, when the excess of aluminium was dissolved out by dilute hydrochloric acid, left an alloy of tungsten and aluminium, Al^4W, as an iron-grey crystalline powder, of specific gravity 5·58, and appearing under the microscope to consist of rhombic prisms. This alloy is not attacked by concentrated acids in the cold, but is oxidised by hot nitric acid, with separation of yellow tungstic acid. Hydrochloric acid dissolves it with deep brown colour. It is decomposed by hot soda-ley, which dissolves the aluminium, and leaves pure tungsten.

Tungsten alloyed with steel in the proportion of 9 or 10 pts. of the former to 90° of the latter, yields an alloy of extraordinary hardness. According to F. A. Bernoulli, (Pogg. Ann. cxi. 573; Jahresb. 1860, p. 153), a very hard tungstiferous *cast-steel* may be obtained by fusing turnings of grey cast-iron with tungsten-trioxide. The reduction of this oxide to metallic tungsten is effected only by the mechanically mixed carbon of the grey cast-iron, not by that which is chemically combined with the iron; accordingly, white cast-iron fused with tungsten-trioxide does not yield tungsten-steel, and after addition of charcoal merely an alloy of tungsten and iron.

Copper, lead, zinc, antimony, bismuth, cobalt, and nickel unite with tungsten, only when the two metals are simultaneously reduced from their oxides. The alloys which they form are so difficultly fusible, that those which contain more than 10 per cent. tungsten do not yield reguline masses; and those which contain volatile metals decompose when strongly heated, leaving nothing but metallic tungsten. Iron is the only metal which alloys with tungsten in all proportions up to 80 per cent. of the latter, with which proportion a mass is formed, not fusible at any attainable temperature. (Bernoulli.)

TUNGSTEN, BROMIDES OF. (Bonnet, J. pr. Chem. x. 206.—Borck, *ibid.* liv. 254; Jahresb. 1851, p. 344.—Riche, Ann. Ch. Phys. l. 5; Jahresb. 1857, p. 185.—Blomstrand, J. pr. Chem. lxxxii. 408; Jahresb. 1861, p. 227.)—Tungsten heated in bromine-vapour unites directly with it, forming products, the composition of which has been variously stated by different chemists. According to Borck, the product consists partly of the tetrabromide, or tungstous bromide, WBr^4; partly of the pentabromide, or tungstoso-tungstic bromide, $W^2Br^{10} = WBr^4.WBr^6$, both of which sublime in black needles, the former, however, being more volatile than the latter, and very deliquescent.—According to Riche, tungsten heated to redness in bromine-vapour, is converted into the hexbromide or tungstic bromide, WBr^6, partly in the form of a fused mass, partly in sublimed needles, of a chestnut-brown colour. This compound, when exposed to moist air, is converted superficially into the violet oxybromide, WBr^4O, and finally into tungstic acid; water converts it immediately into tungstic acid, with brisk effervescence.—According to Blomstrand, the product of the action of bromine-vapour on heated tungsten consists mainly of the pentabromide, W^2Br^{10} (probably resulting from the combination of WBr^4 and WBr^6), mixed, if air and moisture have not been excluded, with the oxybromides, WBr^4O and WBr^2O^2. The black needles, described by Borck as the tetrabromide, consist, according to Blomstrand, of the former of these oxybromides.

The pentabromide, or tungstoso-tungstic bromide, W^2Br^{10}, after repeated tion, has a bluish-black colour; it boils and sublimes near its melting-point, giving off a dark purple-red vapour, which, on cooling, condenses to a compact crystalline mass, or to shining quadratic prisms. In contact with water or moist-air, it is converted into hydrobromic acid and blue oxide of tungsten, W^2O^5. Alkalis dissolve it, without evolution of hydrogen. When heated in contact with the air, it is converted into the oxybromide, WBr^2O^2, which sublimes. (Borck.)

Oxybromides.—Two of these compounds are known, derived from tungstic oxide, WO^3, by replacement of 1 and 2 at. oxygen by equivalent quantities of bromine.—*Tungstic dioxybromide*, WBr^2O^2 or $WBr^6.2WO^3$, first observed by Bonnet, is formed, together with the pentabromide, in the first stage of the reaction of bromine on metallic tungsten when air is not completely excluded; and in a purer state by the action of bromine on the dioxide. It forms yellow crystalline scales, of the colour of brass or mosaic gold. It is infusible, is resolved by heat into tungstic oxide and tungstic monoxybromide, and converted by water into tungstic acid. (Blomstrand.)

The *monoxybromide*, $WBr^4O = 2WBr^6.WO^3$ (described by Borck as the tetrabromide, p. 898), is best obtained by the action of bromine, at a gentle heat, on sulphide of tungsten (prepared in the wet way), or upon a mixture of tungstic oxide and charcoal; it likewise invariably occurs, as an intermediate product, when the pentabromide and the dioxybromide are simultaneously produced. Its colour is very much like that of the pentabromide, only of a lighter black-brown; its vapour is brown-red; it crystallises in woolly needles, and yields tungstic acid with water. (Blomstrand.)

The compound $W^2Br^{10}.W^2O^5$, described by Bonnet, does not appear to exist.

TUNGSTEN, CHLORIDES OF. (Wöhler, Pogg. Ann. ii. 345.—Malaguti, Berz. Jahresb. xv. 103.—H. Rose, *ibid.* xviii. 200.—Borck, J. pr. Chem. liv. 254; Jahresb. 1851, p. 345.—Riche, Ann. Ch. Phys. [3], l. 5; Jahresb. 1856, p. 372; 1857, p. 184.—Blomstrand, J. pr. Chem. lxxxii. 408; Jahresb. 1861, p. 228.—Forcher, Wien. Akad. Ber. xliv. 159; Jahresb. 1861, p. 232.—Debray, Compt. rend. lx. 820; Jahresb. 1865, p. 212.)—Chlorine, like bromine, acts directly upon tungsten, forming products, the composition of which has been variously stated by different chemists. According to recent investigations, however, the compounds obtained by heating metallic tungsten in dry chlorine-gas, are WCl^6 and W^2Cl^{10}, analogous to the bromides; but the hexchloride is more easily obtained in the separate state than the hexbromide, apparently because a lower temperature is sufficient for its formation. If oxygen is present, oxychlorides are also formed, analogous to the oxybromides above described. According to Wöhler and Borck, the tetrachloride, WCl^4, is obtained, as a dark-red compound, by heating tungsten in chlorine-gas; but, according to Blomstrand, this red product is obtained only when oxygen is present, and is really an oxychloride; the tetrachloride, indeed, does not appear to exist, at least in the separate state, not being formed even when one of the higher chlorides is heated in hydrogen-gas (Blomstrand). Riche, on the other hand, states that it is produced in this manner, but is very difficult to obtain pure, being easily resolved into the hexchloride and metallic tungsten.

Hexchloride of Tungsten, or *Tungstic Chloride*, WCl^6.—This compound is formed, together with the following, when tungsten burns in chlorine-gas; in smaller quantity also by heating sulphide of tungsten in chlorine; and, together with oxychlorides, by the action of chlorine on an ignited mixture of tungstic oxide and charcoal. It is less volatile than the pentachloride and oxychlorides, which may therefore be removed from it by sublimation. It forms dark-violet scales, or fused crusts, having a blackish-grey colour and bluish metallic iridescence; by careful sublimation it may be obtained in blackish-violet needles having a metallic aspect. It melts at 183° (Cahours), at 180° (Forcher), to a black liquid, and yields a dark-red vapour (Forcher); reddish-yellow (Blomstrand); it decrepitates on cooling (Blomstrand). The vapour-density, taken at the heat of boiling mercury, is, according to Debray, 11·50; at the heat of boiling sulphur, 11·86; the calculated density for a two-volume condensation is 13·75, which is considerably higher than the experimental numbers. Debray observes, however, that it is very difficult to obtain the hexchloride quite free from pentachloride (which has a lower vapour-density) even by repeated sublimation in chlorine-gas.* The hexchloride, heated in contact with the air, is converted into cinnabar-red flocks of WCl^4O, and soft yellowish-white flocks of hydrated tungstic acid, $WH^2O^4.H^2O$, or $WO^3.2H^2O$; in moist air, or in contact with water, it is completely resolved into hydrochloric and tungstic acids. It dissolves in alkalis, forming tungstates; with alcohol it yields ethylic chloride and blue tungsten-oxide, W^2O^5, which, in contact with the air, is quickly converted into yellow tungstic oxide. (Forcher.)

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* J. Persoz (Ann. Ch. Phys. [4], i. 93; Jahresb. 1863, p. 213) regards tungsten as a metal belonging to the arsenic and antimony group, its oxides being represented by the formulæ Tu^2O^3, Tu^2O^4, Tu^2O^5, the chlorides and bromides by corresponding formulæ, and the atomic weight of the metal being 153·3. According to this view, the vapour-density of tungstic chloride, $TuCl^5$, should be $\frac{153 \cdot 3 + 5 \,.\, 35 \cdot 5}{2} \times 0 \cdot 0693 = 11 \cdot 46$, which agrees very nearly with Deville's determination.

The *Pentachloride*, or *Tungstoso-tungstic Chloride*, $W^2Cl^{10} = WCl^4.WCl^6$, is produced by the combustion of metallic tungsten in chlorine, and in smaller quantity by heating the sulphide in chlorine, mixed in both cases with the hexchloride, from which, and from the oxychloride formed at the same time, if moisture is present, it may be separated by sublimation, as its boiling-point lies midway between that of the hexchloride and that of the oxychloride (Forcher). The pentachloride is likewise obtained by gently heating nitride of tungsten in chlorine-gas, and by the action of chlorine on an ignited mixture of tungetic oxide and charcoal.

Pentachloride of tungsten forms dark-red needles, or larger crystals of a purple-red colour. It is more volatile than the hexchloride, melts to dark-red drops, and its vapour, which resembles nitrous anhydride, quickly condenses in soft crystalline masses. By water or moist air it is converted into yellowish-green tungstic acid; alkalis dissolve it slowly, with evolution of hydrogen, and transient-blue coloration, forming solutions of tungstates. (Forcher.)

According to Blomstrand, on the other hand, the pentachloride is much less volatile than the hexchloride, and to obtain it pure, the mixture of pentachloride and hexchloride, produced as above, must be heated in an atmosphere of hydrogen; care being taken that the heat does not rise too high, in which case metallic tungsten would be separated. The pentachloride thus obtained may be resublimed in hydrogen-gas, or better in carbonic anhydride. Its colour is like that of the hexchloride, but of a darker blackish-grey, without the violet tint. It melts and volatilises much less easily than the hexchloride; yields a greenish-yellow gas; crystallises readily in shining blackish needles; and solidifies from fusion in the crystalline form. Water decomposes it, with considerable rise of temperature, and separation of a blue-black oxide, while the liquid assumes a deep greenish-yellow colour, which it loses after some time, and more quickly when heated, depositing a greenish precipitate. The same appearances, but with deeper colours, are produced by treating the compound with alkalis or with hydrochloric acid.

It is clear, from the preceding statements, that the so-called pentachlorides obtained by Blomstrand and by Forcher were not identical. It is most probable that Forcher's compound is the true pentachloride, inasmuch as Riche (Jahresb. 1856, p. 373), by heating the hexchloride in hydrogen-gas, obtained, not the pentachloride, but the tetrachloride, WCl^4, though he states that this compound is very difficult to prepare in a definite state, being easily resolved, by too strong a heat, into metallic tungsten and the hexchloride. Altogether the chemistry of the chlorides and bromides of tungsten is still in a very unsatisfactory state, and requires further investigation.

Oxychlorides.—Two of these compounds are known, analogous to the oxybromides, and producible by similar reactions.—*Tungstic dioxychloride*, WCl^2O^2, or $WCl^6.2WO^3$, is most easily prepared by heating the dioxide in chlorine-gas; it is also produced, in considerable quantity, when a mixture of the trioxide and charcoal is ignited in chlorine-gas, especially when the proportion of charcoal to tungstic oxide is as 5 : 1 or 4 : 1. Blue oxide of tungsten also yields this compound when heated in chlorine, either alone or with charcoal; and it is even produced, though in small quantity and impure, when dry chlorine is passed over native wolfram, finely pulverised and ignited (Forcher). The dioxychloride forms lemon-yellow or deep golden-yellow flocks, or shining scales, which volatilise between 265° and 267°, in vapours of a deep but pure yellow colour (colourless, according to Blomstrand). It is converted, slowly by moist air, more quickly by water, into hydrochloric acid and yellow hydrated tungstic acid, $WH^2O^4.H^2O$. Alkalis dissolve it, forming tungstates. (Forcher.)

The *monoxychloride*, WCl^4O, or $2WCl^6.WO^3$, is formed when the preceding compound is heated, the condition essential to its formation being not so much a high temperature, as a sudden raising of the heat above 140°. It is also invariably produced, together with the yellow dioxychloride, in the processes above given for the preparation of the latter, and when tungsten or the sulphide is burnt in chlorine-gas, the presence of air or moisture not being completely excluded. It is of a cinnabar or scarlet colour, but sometimes crystallises in slender needles of a lighter red tint, or in orange-yellow flocks made up of slender crystals; in fused crusts it has a carmine colour. It is the most fusible and volatile of all the chlorine-compounds of tungsten, and forms a deep reddish-yellow vapour, which, in contact with the air, is converted into yellowish-white hydrated tungstic acid. By water and moist air, it is quickly converted into hydrochloric and tungstic acids, and by alkalis into a tungstate. (Blomstrand; Forcher.)

The vapour-density of this oxychloride was found by Debray to be 10·74 at the temperature of boiling mercury, 10·27 at that of boiling sulphur. The density, calculated from the formula WCl^4O, for a two-volume condensation, is 11·86; according to the formula and atomic weight proposed by Persoz (footnote, p. 899), it is 9·87.

TUNGSTEN, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions.*—All tungsten-compounds form colourless beads with borax and phosphorus-salt, in the outer blowpipe-flame. With borax, in the inner flame, they form a yellow glass, if the quantity of tungsten is somewhat considerable, but colourless with a smaller quantity. With phosphorus-salt in the inner flame they form a glass of a pure blue colour, unless metallic oxides are present, which modify it; in presence of iron, the glass is blood-red, but the addition of metallic tin renders it blue.

2. *Reactions in Solution.*—The only soluble compounds of tungsten are the tungstates of the alkali-metals and alkaline earth-metals, most of the metatungstates (formed from ordinary tungstates by addition of tungstic acid or abstraction of part of the base), and certain sulphotungstates. Insoluble tungsten-compounds may be decomposed by fusion with alkaline carbonate and nitrate, whereby an alkaline tungstate is formed, which may be dissolved out by water. The behaviour of tungsten-solutions towards many reagents, differs according as the solution contains ordinary tungstic acid or metatungstic acid, the metatungstates being more soluble than the corresponding tungstates; but the following characters are common to both modifications:—

1. A soluble tungstate, supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic acid, yields, on the introduction of a piece of *zinc*, a beautiful blue colour, arising from the formation of blue oxide of tungsten; this effect is not produced with nitric, tartaric, or citric acid.—A soluble tungstate, mixed with *sulphide of ammonium*, and then with excess of acid, yields a light-brown precipitate of tungstic sulphide, soluble in sulphide of ammonium.—*Sulphydric acid* does not precipitate the acidulated solution of a tungstate, but turns it blue, owing to the formation of the blue oxide. These characters, together with the blowpipe-reactions, are sufficient to distinguish tungsten from all other metals. The distinguishing characters of tungstates and metatungstates will be described further on (pp. 905, 912).

3. *Estimation and Separation.*—Tungsten is always estimated in the form of tungstic oxide, WO^3. When tungstic acid is present in a solution not containing any other fixed substance, it is sufficient to evaporate to dryness, and ignite the residue. The tungstic oxide is then obtained in a state of purity, and contains 79·3 per cent. of the metal. Tungstous oxide, WO^2, is easily converted into tungstic oxide by fusion with carbonate of sodium.

The best method of separating tungstic acid from the fixed alkalis is to treat the solution, after exact neutralisation with nitric acid, with a solution of *mercurous nitrate*. Mercurous tungstate is then precipitated, and the mercury may be expelled from the dry precipitate by careful ignition in a good draught.

The separation of tungstic acid from the earths may be effected by decomposing the compound with *nitric acid*, and treating the decomposed mass with *carbonate of ammonia*, which dissolves the tungstic acid.

Tungstic acid may be readily separated from many metallic oxides—such as the oxides of iron, manganese, nickel, cobalt, lead, &c.—by fusing the whole with *carbonate of sodium*, and digesting the fused mass with water, which dissolves the tungstic acid, and leaves the oxides undissolved.

From titanic, tantalic, and niobic acids, tungstic acid is separated by *ammonia*, which dissolves only the latter. The separation is facilitated by addition of *ammonium-sulphide*. If, however, the substance containing these acids has been ignited, mere digestion in ammonia, or sulphide of ammonium, will not dissolve the tungsten: in this case it is best to fuse the mixture with sulphur and carbonate of sodium, whereby the tungsten will be converted into soluble sulphotungstate of sodium.

The separation of tungstic from chromic acid may be effected by treating the solution with excess of *hydrochloric acid*, and boiling with *alcohol*. The chromic acid is thereby reduced to chromic oxide, which may be precipitated by ammonia, the tungstic acid remaining in solution.

To separate tungstic from molybdic acid, it is best to dissolve the two in an alkali, add tartaric acid and excess of hydrochloric acid, which produces no precipitate, and throw down the molybdenum as sulphide by *sulphydric acid*.

From silicic acid, tungstic acid may be separated by fusing the mixture with *acid sulphate of potassium*, and digesting the fused mass with water, which will dissolve the tungsten as alkaline tungstate, and leave the silica. The tungstic acid may then be precipitated from the solution by mercurous nitrate. Tungsten has not, however, been found in any natural silicate.

The separation of tungsten from tin is especially important, as wolfram is often associated with tin-ores, and the two metals likewise occur together in many tantalites and columbites. When stannic and tungstic acid exist together in solution, they are easily separated by sulphydric acid, which precipitates the tin from the acidulated liquid as stannic sulphide, and leaves the tungsten in solution. When stannic and tungstic oxides are mixed together in the solid state, the separation may be effected by igniting a weighed quantity of the mixture in a covered porcelain crucible, and passing a stream of hydrogen-gas into the crucible, through a hole in the cover. The loss of weight thereby occasioned is about equal to that which would correspond to the complete reduction of the tin-oxide to metal, and of the trioxide of tungsten to dioxide. The ignited residue is then boiled with hydrochloric acid, the tin is precipitated from the filtered solution by hydrochloric acid, and the precipitated sulphide is converted by roasting into stannic oxide. Lastly, the dioxide of tungsten is converted, by ignition in the air, into trioxide, and the latter is weighed. The separation cannot be effected by fusing the mixture with acid sulphate of potassium (H. Rose and Dexter, Pogg. Ann. xcii. 335; Jahresb. 1854, p. 731). According to Rammelsberg (Pogg. Ann. cxx. 66; Jahresb. 1863, p. 678), the separation effected by the preceding method is not complete, unless the heat applied is strong enough to reduce the tungsten as well as the tin to the metallic state, and in that case a small quantity of tin is volatilised. He recommends, as a better method, to ignite the mixture of the two oxides repeatedly, and till no more loss of weight takes place, with 6 or 8 pts. of sal-ammoniac. To prevent the deposition of stannic oxide on the outside of the crucible, it should be enclosed within a larger one, and heated rather quickly. The residual tungstic oxide is finally ignited in contact with the air.

4. *Atomic Weight of Tungsten.*—The older determinations of the atomic weight of this metal, by Berzelius and others, did not lead to correct results. Schneider (Ann. Ch. Pharm. lxxvii. 261), by reducing tungstic oxide, WO^3, in a current of hydrogen, found that 100 pts. of the oxide yielded 79·316 pts. of metallic tungsten; and on reoxidising the metal, he found that 79·327 pts. of tungsten yielded 100 pts. of the trioxide. The mean of these results gives W = 184·12. Marchand (*ibid.* lxxvii. 261), by similar experiments of reduction and oxidation, found, as a mean value, W = 184·1; Borck (J. pr. Chem. liv. 254) found, in like manner, the number 184; and the same result has been obtained by Dumas (Ann. Ch. Pharm. cxiii. 23). This last number may be regarded as the true atomic weight of tungsten, supposing, as most of the chemical relations of tungsten seem to show, that its highest oxide has the composition WO^3, and the corresponding chloride WCl^6.

The proposal of Persoz to regard tungstic oxide as Tu^2O^3, the corresponding chloride as $TuCl^3$, the atomic weight of tungsten being 153·3, has already been noticed (p. 899). The agreement of the vapour-density of tungstic chloride calculated from this formula with Debray's experimental number, is certainly remarkable; but, on the other hand, the specific heat of the metal, as determined by Regnault, agrees better with the atomic weight 184 (according to the law of Dulong and Petit) than with 153·3 (see HEAT, iii. 30); moreover the composition of the tungsten-compounds is, on the whole, more conveniently represented by the ordinary formula, than by those suggested by Persoz.

TUNGSTEN, FLUORIDE OF. Tungstic oxide, after ignition, is but sparingly dissolved by hydrofluoric acid; precipitated tungstic acid forms, with hydrofluoric acid, a yellow milky liquid, soluble in a large quantity of water. The solution, when slowly evaporated, yields a yellow syrup, which at a higher temperature gives off a portion of its acid, and solidifies to a greenish fissured mass. This mass is not decomposed by ignition in a close vessel; it redissolves imperfectly in water, forming a milky liquid; the insoluble part consists of tungstic acid, which retains a portion of the hydrofluoric acid so obstinately, that the latter can only be expelled by igniting the tungstic acid with lumps of ammonium-carbonate. The solution contains tungstic acid, with excess of hydrofluoric acid. (Berzelius.)

Tungstic fluoride, WF^6, forms, with the more basic metallic fluorides, compounds which have not yet been isolated, and are known only in combination with tungstates (Berzelius). These double oxyfluorides, which are produced by treating tungstates with hydrofluoric acid, appear to be isomorphous with the corresponding fluosilicates, fluostannates, and fluotitanates. Thus cupric oxyfluotungstate, $CuWO^2F^4$, and cupric fluotitanate, $CuTiF^6$, form isomorphous compounds with fluoride of ammonium; whence it appears as if oxygen could, in certain cases, replace fluorine atom for atom, although the ratio of the atomic weights of these elements is not the same as that of their equivalents. (Marignac, Ann. Ch. Pharm. cxxv. 362; Jahresb. 1862, p. 144.)

TUNGSTEN MINERAL. Native tungstate of calcium, also called scheelite (p. 907).

TUNGSTEN, NITRIDE OF. When either of the chlorides of tungsten is placed at the sealed end of a long glass tube, and in front of it a few dried lumps of sal-ammoniac, the empty part of the tube then heated to redness, and the heat gradually extended to the closed end, so that the two salts may be volatilised and mix in the gaseous form at a red heat, double decomposition takes place; and after the excess of sal-ammoniac has been removed, the entire inner surface of the tube is found to be covered with a black specular semimetallic coating, which may be separated, partly in brittle crusts, partly as a black powder. This product consists either of nitride of tungsten, or of a compound of that substance with an amide of tungsten, called by Wöhler tungsten-nitretamide, and containing either $2WN^2.W(NH^2)^2$, or $W^2N^2.2W(NH^2)^2$. It gives off a large quantity of ammonia when fused with potash, and is converted into tungstic oxide by ignition in the air. By the action of ammonia-gas on tungstic oxide, at a moderate red heat, compounds are formed containing nitride, amide, and oxide of tungsten. When finely-divided tungstic oxide, spread in a thin layer on the inside of a glass tube, is heated in dry ammonia-gas, tungsten-nitretamidoxide, $3WN^2.2W(NH^4).2WO^3$, is formed, as a black substance which is not decomposed by acids or alkalis, gives off ammonia when heated alone, and when heated in the air, burns with vivid glow to yellow tungstic oxide. (Wöhler, Ann. Ch. Pharm. lxxiii. 190; cv. 258; Jahresb. 1850, p. 303; 1858, p. 158.)

TUNGSTEN, OXIDES OF. Tungsten forms three oxides—viz. WO^2, WO^3, and W^2O^5—neither of which exhibits basic properties, so that there are no salts of tungsten in which the metal replaces the hydrogen of an acid, or takes the electropositive part. The dioxide forms a definite compound with soda, and the trioxide exhibits decided acid tendencies, uniting with basic metallic oxides, and forming definite crystallisable salts called tungstates. The oxide, W^2O^5, may be regarded as a compound of the other two, that is as a tungstate of tungsten, $WO^2.WO^3$.

Dioxide of Tungsten, or **Tungstous Oxide,** WO^2.—This oxide is obtained as a brown powder when tungstic oxide is reduced by hydrogen at a temperature not exceeding low redness. Tungstic oxide may also be deprived of oxygen in the wet way, by pouring diluted hydrochloric acid over it, and placing zinc in the liquor: the trioxide then gradually changes into the dioxide, in the form of brilliant crystalline plates of a copper-red colour. No saline compounds of this oxide with acids are known. When digested in a strong solution of potassic hydrate, it dissolves, with disengagement of hydrogen-gas and formation of potassic tungstate.

A *tungstite of sodium*, $Na^2W^2O^5 = Na^2O.2WO^2$, is obtained by adding to fused tungstate of sodium as much tungstic oxide as it will take up, and exposing the mass, at a red heat, to hydrogen-gas. After dissolving out the neutral undecomposed tungstate by water, the tungstite remains in golden-yellow scales and regular cubes, possessing the metallic lustre and a striking resemblance to gold. This compound is not decomposed by sulphuric, nitric, or nitromuriatic acid, or by alkaline solutions, but yields to hydrofluoric acid. It cannot be prepared by uniting soda directly with the dioxide.

Trioxide of Tungsten, Tungstic Oxide or **Anhydride,** WO^3.—This oxide occurs native as tungstic ochre, wolfram-ochre, or wolframine, accompanying wolfram or other ores of tungsten, in Cumberland, at St. Leonard near Limoges, in Mourne County, Connecticut, and in Cabarras County, North Carolina; sometimes in cubes, sometimes pulverulent and earthy, of a bright-yellow or yellowish-green colour.

Tungstic oxide is prepared from scheelite (native tungstate of calcium), or from wolfram:

1. Finely-pulverised scheelite is decomposed by nitric or hydrochloric acid; the soluble nitrate or chloride of calcium is washed out with water, and the remaining tungstic acid is ignited.

2. Finely-pulverised wolfram is repeatedly digested with strong hydrochloric acid, at last with addition of a little nitric acid, to dissolve out the iron and manganese, the tungstic acid which remains is washed and dissolved in aqueous ammonia; the solution evaporated to dryness; and the residual acid ammonium-salt heated in contact with the air: tungstic oxide then remains in pale-yellow scales.—3. One pt. of pulverised wolfram is fused with 2 pts. carbonate of potassium; the fused mass is digested with water; the filtered solution mixed with sal-ammoniac and evaporated; and the residue is ignited in a crucible, and then treated with zinc and hydrochloric acid, whereby brown dioxide of tungsten is produced, which, when ignited in the air, yields the pure trioxide (Wöhler).—4. Pulverised wolfram is fused for an hour with 2 pts. chloride of calcium; the fused mass is treated with water, which leaves tungstate of calcium undissolved; this salt is decomposed by boiling with hydrochloric acid; the residual tungstic acid is dissolved in ammonia (to free it from silica); and the ammonium-salt, obtained on evaporating the filtrate, is ignited in contact with the air. (Wöhler.)

The solution of alkaline tungstate obtained by either of the preceding methods may also be mixed with mercurous nitrate, whereby a precipitate of mercurous tungstate is obtained, which on ignition leaves pure tungstic oxide.

Anhydrous tungstic oxide is a lemon-yellow or sulphur-yellow powder, darker or lighter according to the mode of preparation. Nordenskjöld, by fusing the tungstic hydrate with borax in a pottery-furnace, obtained the anhydrous oxide in small transparent tables or short prisms belonging to the trimetric system. Debray (Compt. rend. lv. 287), by strongly igniting a mixture of sodic carbonate and tungstate in a current of hydrochloric acid gas, obtained the tungstic oxide in octahedral crystals—some small and translucent with yellowish colour, others larger, black, and opaque.

Tungstic oxide has a specific gravity of 5·27 (Herapath), 6·12 (d'Elhujar), 7·14 (Krosten). It is tasteless, insoluble in water and in most acids, only slightly soluble in strong hydrochloric and in hydrofluoric acids. When heated, it becomes transiently darker and greenish, at very high temperatures, but, according to Bernoulli (Jahresb. 1860, p. 153), the greenish and the yellow oxides have exactly the same composition. Tungstic oxide melts at the heat of a forge-fire, and volatilises quickly when heated on charcoal before the oxyhydrogen-blowpipe. When heated for ten or twenty minutes before the oxyhydrogen-blowpipe, in a covered platinum-crucible, it forms a crystalline crust, the surface of which exhibits crystals apparently formed by sublimation; no sublimate is, however, formed on the sides of the crucible. In hydrochloric acid gas, tungstic oxide volatilises easily, forming a sublimate of pale-yellow stellate needles. (Schafarik.)

Tungstic oxide turns greenish on exposure to light, probably in consequence of the reducing action of organic particles in the air. According to Liesegang (Jahresb. 1865, p. 214), when exposed to light in contact with *organic substances*, it is reduced to blue oxide. When heated to redness, in contact with *charcoal* or *hydrogen*, it is reduced to dioxide or metal, according to the temperature and the duration of the action; by ignition with *potassium* or *sodium*, it is reduced to metal; by ignition in dry *ammonia-gas*, it is converted into oxynitretamide of tungsten (p. 903), by heating with sulphur to blue oxide.—When it is heated with *pentachloride of phosphorus*, oxychloride of phosphorus passes over, together with small quantities of tungstic chloride and oxychloride, WCl^4O; the greater part of the tungsten, however, remains in the residue which, when treated with water, yields hydrochloric acid and a mixture of tungstic oxide with the blue oxide. (Gerhardt and Chiozza, Ann. Ch. Pharm. lxxxvii. 290; Jahresb. 1853, p. 395; see also Schiff, *ibid.* 1857, p. 106; Weber, *ibid.* 1859, p. 79.)

Tungstic oxide is also reduced by *zinc* and *hydrochloric acid*, by *stannous chloride*, or by boiling with *organic bodies* and water—first to the blue oxide, then, by further reduction, to the brown dioxide.

TUNGSTIC ACID.—Tungstic oxide dissolves in aqueous alkalis or alkaline carbonates, slowly in the cold, more quickly at the boiling heat, forming solutions of tungstates; and, on precipitating the hot solutions of these salts with an acid, tungstic monohydrate, or tungstic acid, $H^2WO^4 = H^2O.WO^3$, is obtained as a yellow precipitate; it dissolves in hydrofluoric acid, and separates from the solution in crystals on evaporation.

By mixing a dilute solution of an alkaline tungstate with hydrochloric, nitric, or sulphuric acid, a white gelatinous precipitate is obtained, having, when air-dried, the composition of tungstic dihydrate or hydrated tungstic acid, $2H^2O.WO^3 = H^2WO^4.H^2O$.—This hydrate is likewise formed by the decomposition of tungstic chloride, or oxychloride, with water; after washing and drying, it is sometimes yellowish-grey and translucent, sometimes black and opaque; when finely pulverised, it is said to dissolve in 200 pts. of boiling, and 300 pts. of cold water. (Anthon, J. pr. Chem. ix. 6.—Riche, Ann. Ch. Phys. [3], l. 5.)

Tungstic acid reddens litmus, and dissolves in aqueous fixed alkalis, and in ammonia.

TUNGSTATES.—Tungstic acid unites with bases in various and often in very unusual proportions. The salts have been examined by Berzelius (Pogg. Ann. iv. 147; viii. 267), Anthon (J. pr. Chem. viii. 399; ix. 6, 8, and 337), Margueritte (J. Pharm. [3], vii. 222), Laurent (Ann. Ch. Phys. [5], xxi. 54), Lotz (Ann. Ch. Pharm. xci. 49; Jahresb. 1854, p. 339), Scheibler (Berl. Akad. Ber. 1860, p. 208; Jahresb. 1860, p. 154), and Marignac (Ann. Ch. Phys. [3], lxix. 5; Jahresb. 1862, p. 143); but the results of these investigations are not very accordant, inasmuch as the salts often differ considerably in composition and properties, according to the mode of preparation adopted. Laurent, from the behaviour of the ammonium-tungstates, was led to admit the existence of five isomeric or polymeric modifications of the tungstates; but from recent investigations, it appears that the number of modifications of tungstic acid and its salts may be reduced to two, viz.:

1. Ordinary tungstic acid, which is insoluble in water, and forms insoluble salts with all metals, except the alkali-metals.

2. Metatungstic acid, which is soluble in water, and forms soluble salts with nearly all metals.

Ordinary Tungstates.

Ordinary tungstic acid forms both neutral and acid salts. The neutral tungstates contain M^2WO^4, or $M^2O.WO^3$; the acid salts were formerly supposed to be either diacid, $M^2O.2WO^3 = M^2WO^4.WO^3$, or triacid, $M^2O.3WO^3 = M^2WO^4.2WO^3$. According to Scheibler, however, the acid tungstates have in general the formula $3M^2O.7WO^3$ $4H^2O$, and may be regarded as double salts composed of sesquitungstates and tetratungstates—*i.e.*, as $2M^2O.3WO^3 + M^2O.4WO^3$, or perhaps of diacid and triacid salts, $2(M^2O.2WO^3) + M^2O.3WO^3$ (according to Persoz, $2M^2O.2H^2O.3Tu^2O^5$). According to Laurent, the empirical formula of the acid salts is $5M^2O.12WO^3.xH^2O$; and according to Marignac, this formula agrees with the analytical results more nearly than that given by Scheibler; but the percentage composition deduced from the one formula differs so little from that given by the other, that it is difficult to decide between the two by analysis. Scheibler's formula, however, which is the more simple of the two, is generally preferred. Marignac designates these salts, which he regards as containing 5 at. basic oxide to 12 at. tungstic anhydride, or 5 at. monatomic metal to 6 at. tungsten, as paratungstates; he finds that the ammonium-salt having this composition cannot be converted into the neutral tungstate by digestion with ammonia. They are produced more easily, and crystallise better, than acid tungstates containing any other proportion of base and acid.

Of the ordinary tungstates, only those of the alkali-metals and magnesium are soluble in water, and these are but sparingly soluble. They may be prepared in the wet way by dissolving tungstic oxide or tungstic acid in alkalis, or alkaline carbonates, most easily at the boiling heat. They are also easily formed by fusing tungstic oxide with the hydrates, carbonates, or acid sulphates of the alkali-metals. They have a bitter metallic taste, and excite an unpleasant feeling in the throat. The insoluble tungstates are prepared by igniting tungstic oxide with metallic oxides or carbonates, or from the soluble salts by precipitation; also by fusing an alkaline tungstate with the corresponding metallic chlorides (chloride of calcium, for example); on exhausting the mass with water, the insoluble tungstate remains in the crystalline state (Manross, Ann. Ch. Pharm. lxxxi. 243; lxxxii. 356, 357). Larger crystals are obtained by adding chloride of sodium to the fused mixture. (Geuther and Forsberg, *ibid.* cxx. 268.—Schultze, *ibid.* cxxvi. 56.)

Those tungstates which are insoluble in water are also, for the most part, insoluble in dilute acids; by heating with concentrated acids, they are decomposed, with separation of tungstic acid (a character by which they are distinguished from the metatungstates); in the case of phosphoric acid, the precipitated tungstic acid dissolves in excess. At ordinary temperatures, tungstates are but imperfectly decomposed by concentrated acids, chiefly because a certain quantity of soluble tungstic acid is formed at the same time (p. 911). Alkaline tungstates in solution are decomposed by sulphuric, hydrochloric, nitric, and acetic acids, the greater part of the tungstic acid being separated as a yellow or white hydrate, which does not dissolve in an excess of the precipitating acid (except phosphoric acid); it dissolves, however, in a large quantity of water.

The precipitate obtained from cold solutions is frequently white, but gradually turns yellow even in the cold, and more quickly when heated. The composition of this white precipitate has been variously stated. Scheele regarded it as pure tungstic oxide, which however is not correct; according to Anthon and Riche, it is the dihydrate, $WO^3.2H^2O$; according to Marignac and others, it contains a basic tungstate, or it is a compound of tungstic acid with the precipitating acid. Whether the precipitate retains alkali or acid depends on the relative quantity of the precipitating acid, the dilution of the liquid, and perhaps also on the temperature.

Insoluble tungstates, whose bases are insoluble in alkaline carbonates, are decomposed by fusion with alkaline carbonate.

Solutions of alkaline tungstates give white precipitates with salts of *barium*, *strontium*, *calcium*, *aluminium*, *zinc*, *lead*, and *mercuricum*; yellowish-white with *mercurous nitrate*; peach-blossom-coloured with *chloride of cobalt*; bluish-white with *nitrate of copper*.—*Stannous chloride* forms a yellowish precipitate, which, when warmed with hydrochloric or sulphuric acid, turns blue, from formation of blue tungsten-oxide.

Ferrocyanide of potassium forms in solutions of alkaline tungstates, after addition of hydrochloric acid, a brown flocculent precipitate, soluble in pure water free from acid (distinction from metatungstates). Solutions of alkaline tungstates are not altered by *tincture of galls*, till an acid is likewise added, in which case a thick chocolate-coloured precipitate is formed. Tungstic acid, previously precipitated by acids, is also coloured brown by tincture of galls. Alkaline tungstates, ignited with *sal-ammoniac*, out of contact with the air, yield a tungstate of tungsten and the alkali-metal, together with a black substance, probably consisting of oxynitretamide of tungsten (p. 903). For the blowpipe-reactions of tungstates, and the reactions of soluble tungstates with zinc and with sulphide of ammonium, see p. 901.

Alkaline tungstates are sometimes used, in place of stannates, as mordants; they are also employed for rendering light fabrics non-inflammable (i. 1102).

TUNGSTATES OF ALUMINIUM.—The *neutral salt*, obtained by precipitating a neutral alkaline tungstate with alum, is white, flocculent, insoluble in water, but soluble in aqueous ammonia and in acids.—The *acid salt*, $Al^2O^3.7WO^3.9H^2O$ (at 100°), obtained by precipitation with an acid tungstate of alkali-metal is curdy, united in resinous lumps, and forms, when dry, a vitreous mass, having a conchoïdal fracture. (Lotz.)

TUNGSTATES OF AMMONIUM.—*a*. The *neutral salt* is formed by digesting tungstic acid or oxide with aqueous ammonia; on evaporating the solution, ammonia is given off, and an acid salt remains.

β. The *sesquiacid salt*, $2(NH^4)^2O.3WO^3.3H^2O = (NH^4)^4H^2(WO^4)^3.2H^2O$, sometimes crystallises from a very concentrated neutral solution of tungstic acid in ammonia, in warty crystals, which give off ammonia in contact with the air, leaving the following salt.

γ. $3(NH^4)^2O.7WO^3.6H^2O = (NH^4)^6H^8(WO^4)^7.2H^2O$.—This salt, to which Marignac assigns the formula $5(NH^4)^2O.12WO^3.11H^2O$, is obtained by slow evaporation of a cold solution of tungstic acid in ammonia (Lotz; Scheibler). It forms vitreous rhombic tables or prisms, acuminated with four faces resting on the edges of the prism. It has a biting bitter taste, reddens litmus slightly, dissolves in 26 to 28 pts. of cold water, is sparingly soluble also in aqueous ammonia, and insoluble in alcohol. The solution gives with nitric acid a white precipitate, which turns yellow gradually in the cold, immediately on boiling. When ignited in a close vessel, it leaves blue oxide of tungsten, and, when ignited in contact with the air, it leaves pure tungstic oxide, which retains the form of the crystals.

When the solution is evaporated by heat, small shining crystals are obtained (oblique, striated, rhombic prisms, according to Marignac), containing $3(NH^4)^2O.7WO^3.3H^2O$ [or, according to Laurent, $5(NH^4)^2O.12WO^3.4H^2O$; according to Marignac, $5(NH^4)^2O.12WO^3.5H^2O$]; they give off 2 at. water at 160°, and are reconverted into the hexhydrated salt by solution in water, and slow evaporation. (Scheibler.)

δ. An *ammonio-trihydric tetratungstate*, $(NH^4)^2O.3H^2O.4WO^3 = (NH^4)^2H^6(WO^4)^4$, is always formed (according to Riche) when a solution of ammonium-tungstate is left to evaporate slowly; and separates at ordinary temperatures in shining laminæ containing 3 at. water; at 40°—50°, in needles containing 2 at. water.

According to Wöhler and Anthon, an acid tungstate of ammonium is produced, with evolution of ammonia, when tungstate of potassium or sodium is boiled with sal-ammoniac. According to Laurent, Lotz, and others, the salt thereby formed is a double tungstate of ammonium and potassium or sodium.

ε. The salt, $2(NH^4)^2O.5WO^3.5H^2O = (NH^4)^4H^6(WO^4)^5.2H^2O$, crystallises on cooling from a solution of the salt *γ*, saturated while hot, in rhombic octahedrons, soluble in 26 to 29 pts. of water. On recrystallising it from water, thin nacreous needles are sometimes formed, containing $2[(NH^4)^3H^5(WO^4)^4].3H^2O$. (Marignac.)

TUNGSTATES OF BARIUM.—*a*. The *neutral salt*, $Ba''WO^4 = BaO.WO^3$, is obtained, in the anhydrous state, by precipitation from the solution of a neutral tungstate of alkali-metal. It is a white powder, insoluble in water, decomposed by the stronger acids, and also by alkaline carbonates, both in the wet and in the dry way. According to Scheibler, the precipitate formed by chloride of barium in a solution of neutral sodium-tungstate is always a mixture of different salts; but the neutral tungstate may be obtained pure by heating the metatungstate with hydrate of barium, or by dropping baryta-water into a moderately dilute and boiling solution of acid tungstate of sodium, $(3Na^2O.7WO^3)$, as long as the resulting precipitate is redissolved; the solution on cooling deposits a double salt, and the cooled mother-liquor yields, with excess of baryta water, a white bulky precipitate, which soon becomes dense and crystalline, and then forms spicular octahedrons of pure neutral barium-tungstate. The salt thus obtained, as well as that prepared from the metatungstate, contains $2Ba''WO^4.H^2O$.—The anhydrous salt is formed, in the dry way, by fusing together 2 pts. sodium-tungstate, 7 pts. barium-chloride, and 4 pts. sodium-chloride, and crystallises in colourless octahedrons, apparently isomorphous with the calcium-salt; they are decomposed by strong nitric acid at the boiling heat only. (Geuther and Forsberg.)

β. *Acid salt*, $3BaO.7WO^3.8H^2O$.—Obtained by precipitation from the acid sodium-salt. White; becomes anhydrous and yellowish by ignition. (Lotz.)

Sodio-baric tungstate, $\left.\begin{matrix}2BaO\\Na^2O\end{matrix}\right\}7WO^3.14H^2O$ (Scheibler), or $\left.\begin{matrix}2BaO\\3Na^2O\end{matrix}\right\}12WO^3.24H^2O$ (Marignac), separates in thin plates on cooling, from a hot solution of acid sodium-tungstate, after addition of baryta-water.

TUNGSTATE OF CADMIUM is obtained in colourless crystals, perhaps isomorphous with the calcium-salt, by fusing 4 pts. sodium-tungstate with 11 pts. cadmium-chloride and 16 pts. common salt (Geuther and Forsberg).—An *ammonio-cadmic tungstate*, $4(3CdO.7WO^3).[3(NH^4)^2O.7WO^3] + 35H^2O$, is obtained, as a white bulky precipitate, on mixing the solutions of acid ammonium-tungstate and cadmium-sulphate. (Lotz.)

Tungstate of Calcium, $Ca''WO^4$, or $CaO.WO^3$, occurs native, as **scheelite** or **tungsten**, in quadratic pyramids P, modified by the faces $2P\infty$ and $\frac{4P2}{2}$, the latter occurring hemihedrally. For P, the length of the principal axis is 1·0858; the angle P : P in the terminal edges = 107° 20′; in the lateral edges = 113° 51′. The crystals cleave indistinctly parallel to P, more distinctly parallel to $2P\infty$. The mineral likewise occurs reniform, with columnar structure, and massive granular. Hardness = 4·5 to 5. Specific gravity = 6 to 6·076. Lustre vitreous, inclining to adamantine. Colour white, inclining to yellow and brown. Streak white. Subtransparent to subtranslucent. Fracture uneven. Brittle. Scheelite is usually associated with crystalline rocks, and is found associated with tin-ore, topaz, fluor-spar apatite, or wolfram, in quartz. It occurs at Caldbeck Fell, near Keswick, in fine crystals; also in Bohemia, Saxony, Hungary, and Sweden, at Coquimbo in Chile, and in Monroe and Huntingdon counties, Connecticut.

Tungstate of calcium may be obtained in crystals, by fusing wolfram with excess of calcium chloride, and boiling out the soluble salts from the slowly-cooled mass (Manross, Ann. Ch. Pharm. lxxxi. 243)—also by heating the amorphous salt with lime in a stream of hydrochloric acid gas (Debray, *ibid.* cxxv. 97). The same salt is obtained by precipitation as a white powder. It is insoluble in pure water, and in acidulated water.

Tungstates of Chromium.—The *neutral salt*, $Cr^2O^3.3WO^3.13H^2O$, obtained by precipitation, is light-green, easily soluble in acids, and turns yellowish-grey in drying.—An *acid salt*, $Cr^2O^3.7WO^3.9H^2O$, obtained by precipitation from the acid ammonium-salt, is a light greyish-green powder, greenish straw-yellow after ignition. (Lotz.)

Tungstate of Cobalt, $CoWO^4$, is obtained in blue-greenish translucent crystals, by fusing 1 pt. sodium-tungstate, 2 pts. cobalt-chloride, and 2 pts. common salt. (Schultze.)

Tungstate of Copper.—The mixture obtained by fusing 2 pts. sodium-tungstate with 3 pts. cupric chloride and 4 pts. common salt, leaves, after treatment with dilute nitric acid, white translucent quadratic pyramids, on which yellowish-brown crystals are implanted. (Schultze.)

Tungstates of Iron.—*a. Ferric tungstate* is obtained, by precipitating ferric chloride with acid ammonium-tungstate, as a cream-coloured powder, which dissolves in tungstate of ammonium on boiling, and in ferric chloride even at ordinary temperatures. Ferric tungstate is also precipitated by ammonia from solution of ferric metatungstate, while an ammonio-ferric tungstate remains dissolved. The same double salt appears to be formed by the action of ammonia on the crude tungstic acid obtained by treating wolfram with nitromuriatic acid. Borck obtained in this manner a double salt containing $Fe^2O^3.5(NH^4)^2O.5WO^3 + 5H^2O$.

β. Ferrous tungstate, $Fe''WO^4$, is formed, by precipitating ferrous sulphate with acid tungstate of ammonium, as a brown precipitate, becoming darker when heated out of contact with the air. The same salt is obtained by fusing 1 pt. tungstate of sodium with 2 pts. ferrous chloride and 1 pt. common salt, in thick, deep black, highly lustrous, opaque crystals, having the form of native wolfram; they are non-magnetic, their powder is of a dark violet-brown colour, and specific gravity = 7·1 (Geuther and Forsberg). Debray, by igniting a mixture of tungstic oxide and ferric oxide in a stream of hydrochloric acid gas, obtained crystals of ferrous tungstate (together with crystals of magnetic iron-ore and tungstic oxide), exactly like those of native wolfram.

Ferroso-manganous Tungstate, $(Fe;Mn)''WO^4$, or $(FeO;MnO).WO^3$.—This is the composition of wolfram, the principal ore of tungsten, which occurs in trimetric crystals having the axes $a : b : c = 0·8231 : 1 : 0·851$. Angle $\infty P : \infty P$ (macr.) = 78° 55′; $\infty\bar{P}2 : \infty\bar{P}2$ = 44° 44′; $\breve{P}\infty : \breve{P}\infty$ (basal) = 80° 48; $\frac{1}{2}\bar{P}\infty : \frac{1}{2}\bar{P}\infty$ = 54° 40′. Observed combination $\infty P . \infty\bar{P}2 . \infty\breve{P}\infty . \frac{1}{2}\bar{P}\infty . \breve{P}\infty . P$. Cleavage parallel to $\infty\breve{P}\infty$. It also occurs lamellar, columnar, and massive granular, the particles being strongly coherent. Hardness = 5 to 5·5. Specific gravity = 7·1 to 7·55. Lustre submetallic. Colour dark-grey or brownish-black. Streak dark reddish-brown. Opaque, sometimes feebly magnetic. According to the proportions of iron and manganese in wolfram, the varieties may be included in three groups, represented by the formulæ $MnWO^4.3FeWO^4$, $MnWO^4.4FeWO^3$, and $MnWO^4.5FeWO^4$.

Wolfram is often associated with tin-ores; also with galena in veins traversing greywacke; also in quartz with native bismuth, tungstate of calcium, pyrites, galena, blende, &c. It occurs in Cornwall and Cumberland, on the island of Rona in the Hebrides, at Limoges in France, and at numerous localities in Saxony and Bohemia; also in the United States. The crystals from Zinnwald, Bohemia, are remarkable as hemitropes. (Dana, ii. 353.)

Geuther and Forsberg have obtained several crystallised tungstates of iron and manganese, by fusing tungstate of sodium with chloride of manganese and chloride of iron in various proportions.

TUNGSTATES OF LEAD.—The *neutral salt*, $Pb''WO^4$, or $PbO.WO^3$, occurs native as scheeletine, a mineral occurring in quadratic crystals, isomorphous with molybdate of lead (iii. 1039). Length of principal axis = 1·5692. Angle P : P in the terminal edges = 99° 42′, in the lateral edges = 131° 30′. The crystals are often indistinctly aggregated. Cleavage imperfect parallel to oP, still more imperfect parallel to P. Hardness = 2·75. Specific gravity = 7·87 to 8·13. Lustre resinous, subadamantine. Colour green, yellowish-grey, brown, and red. Streak uncoloured. Faintly translucent. The mineral occurs at Zinnwald in Bohemia, with quartz and mica; in Carinthia with molybdate of lead; and in Chile, probably near Coquimbo.

Neutral tungstate of lead is produced artificially, as a white powder, by precipitation from the neutral sodium-salt. By fusing tungstate of sodium with 4·7 pts. of chloride of lead in a closed crucible, a dark-green mass is obtained, having its cavities lined with colourless shining crystals of tungstate of lead. (Manross, Ann. Ch. Pharm. lxxxii. 357.)

The *acid lead-salt*, $3PbO.7WO^3.10H^2O$, is formed, on mixing acid ammonium-tungstate with a soluble lead-salt, as a white, flocculent, afterwards pulverulent precipitate, insoluble in water, dilute nitric acid, aqueous nitrate of lead, or tungstate of ammonium, but soluble in caustic soda. It gives off 7 at. water at 100°.

TUNGSTATES OF LITHIUM.—The *neutral salt* is prepared with tungstic acid and carbonate of lithium, either in the wet or in the dry way; and crystallises from the aqueous solution in oblique rhomboïdal prisms (C. Gmelin), or in octahedrons (Anthon), having a rough bitter taste and alkaline reaction, easily soluble in water.—The *acid salt*, $3Li^2O.7WO^3.19H^2O$, or $Li^6H^8(WO^4)^7.15H^2O$ (Scheibler), is prepared like the corresponding sodium-salt, avoiding an excess of tungstic acid, which would lead to the formation of a metatungstate. It crystallises in large monoclinic prisms and tables, permanent in the air, somewhat less soluble than the neutral salt; melts only at a high temperature, and solidifies to a porcelain-like mass on cooling.

TUNGSTATES OF MAGNESIUM.—Solutions of magnesium-salts are not precipitated by neutral tungstates of alkali-metal. By boiling magnesium-carbonate and tungstic oxide with water, a solution is obtained which on evaporation yields small shining scales, permanent in the air, having a harsh bitter taste, and easily soluble in water (Anthon).—The *neutral salt*, $Mg''WO^4 = MgO.WO^3$, is obtained by fusing 1 pt. sodium-tungstate, 2 pts. magnesium-chloride, and 2 pts. common salt, and boiling out the more soluble salts, in colourless, octahedral and prismatic crystals, which are gradually decomposed by heating with strong nitric acid: they are isomorphous with the neutral calcium-salt. (Geuther and Forsberg.)

Ammonio-magnesian Tungstates.—The salt $\left.\begin{matrix}2MgO\\(NH^4)^2O\end{matrix}\right\}7WO^3.10H^2O$ separates gradually, in small nacreous crystals, from a mixture of the hot concentrated solution of the tungstates of magnesium and ammonium.—Another double salt, $\left.\begin{matrix}3MgO\\2(NH^4)^2O\end{matrix}\right\}12WO^3.24H^2O$, separates, on cooling, as a crystalline powder, from a boiling solution of acid ammonium-tungstate mixed with sulphate of magnesium.

TUNGSTATES OF MANGANESE.—Manganous salts yield a white or yellowish precipitate with neutral or acid tungstate of ammonium.—The *neutral salt*, $MnWO^4$, prepared in the dry way like the magnesium-salt, forms thick, light garnet-brown, highly lustrous, rhombic crystals, of specific gravity 6·7; at the same time there are formed yellow needles having the same composition as the preceding (Geuther and Forsberg).—The *acid salt*, $3MnO.7WO^3.11H^2O$, is a gummy yellowish precipitate, which gives off only 3 at. water at 100°. (Lotz.)

The tungstates of iron and manganese have been already described (p. 907).

TUNGSTATES OF MERCURY.—*a. Mercuric Salts.*—A *basic salt*, $3HgO.2WO^3$, is obtained by precipitating a boiling solution of mercuric chloride with an insufficient quantity of potassic tungstate. It is a white heavy powder, insoluble in water.—An *acid salt*, $2HgO.3WO^3$, is obtained, as a white insoluble body, by precipitating a solution of neutral mercuric nitrate with neutral tungstate of potassium. Both these salts are decomposed by boiling alkalis, with separation of mercuric oxide, and leave tungstic oxide when ignited.—An *ammonio-mercuric tungstate*, $Hg''(NH^4)^2(WO^4)^2.H^2O$, is obtained, as a heavy white precipitate, on mixing mercuric nitrate with acid tungstate of ammonium.

β. Mercurous tungstate, $Hg^2O.WO^3$, or Hg^2WO^4 (Anthon), is formed, on adding mercurous nitrate to an alkaline tungstate, as a yellow precipitate, becoming dark-yellow when dry, insoluble in water, leaving tungstic oxide when ignited. The insolubility of this salt renders it available for the separation and estimation of tungstic acid.

Tungstate of Molybdenum is precipitated from a mixture of molybdic chloride and tungstate of ammonium, on addition of sal-ammoniac. After washing with sal-ammoniac, then with alcohol, and drying, it is a dark-purple body, permanent in the air, and easily soluble in water; ammonia, added to the aqueous solution, throws down an ammonio-molybdic tungstate. The solution of molybdic tungstate oxidises and becomes decolorised on exposure to the air, and deposits molybdic tungstic acid. (Berzelius.)

Tungstate of Nickel, $3NiO.7WO^3.14H^2O$, obtained on adding sulphate of nickel to acid tungstate of ammonium, as a light-green precipitate, which unites into lumps of the consistence of turpentine (Lotz). By fusing 1 pt. sodium-tungstate with 2 pts. nickel-chloride and 2 pts. common salt, the neutral tungstate of nickel, $NiWO^4$, is obtained in well-defined, brown, highly lustrous, translucent crystals, having the aspect of zinc-blende. (Schultze, Ann. Ch. Pharm. cxxxi. 56.)

Tungstates of Potassium.—These salts are formed by adding pulverised wolfram to about an equal weight of fused carbonate of potassium, continuing the heat for some time; on boiling the cooled and pulverised mass with water, evaporating the filtrate to dryness, and treating the residue with lukewarm water, the neutral salt dissolves, while the acid salt remains behind.

The *neutral salt*, K^2WO^4, or $K^2O.WO^3$, crystallises from a hot saturated solution on cooling, or on evaporation by heat, in anhydrous, thin, needle-shaped, hexagonal crystals, easily soluble in water, decrepitating when heated, and melting at a red heat (Marignac).—The *monohydrated neutral salt*, $K^2WO^4.H^2O$, is obtained by gradually adding 45 pts. of tungstic oxide to a concentrated solution of potassic carbonate heated to 60°—80°, and crystallises from the hot filtered solution on cooling, in needle-shaped, sometimes aggregated crystals. It has a rough and somewhat bitter taste, is easily soluble in water, insoluble in alcohol; on pouring alcohol on the aqueous solution, the salt crystallises at the surface of contact.—The *dihydrate*, $K^2WO^4.2H^2O$, crystallises by evaporation of the solution over oil of vitriol, at a temperature not above 10°, in large, shining, oblique, rhombic prisms or tables, which quickly effloresce in dry, and deliquesce in moist air.—The *pentahydrate*, $K^2WO^4.5H^2O$, crystallises, according to Anthon, in colourless six-sided prisms, but the conditions of its formation are not particularly stated.

The *acid salt* ($K^2O.2WO^3.2H^2O$, according to Anthon and Riche; $3K^2O.7WO^3.6H^2O$, according to Scheibler; $5K^2O.12WO^3.11H^2O$, according to Laurent and Marignac) is formed by adding tungstic acid to the neutral salt, in fusion or aqueous solution; or by treating this solution with any other acid; or by passing a stream of carbonic anhydride through it. The salt is then deposited as a crystalline powder, consisting of iridescent scales, while metatungstate of potassium remains in solution. The acid tungstate tastes like the neutral salt; it has an acid reaction, dissolves, according to Riche, in 46 pts. cold and 15 pts. boiling water; according to Marignac, in 71 pts. water at 20°. When, however, a saturated solution is prepared by boiling an excess of the salt with water for several days, the cooled solution contains 1 pt. of the salt, after one day, dissolved in 5·6 pts. water; after 26 days, in 11·9 pts. water; after 153 days, in 15·6 pts. water—this last degree of solubility remaining unaltered for six months (Marignac). The salt is insoluble in alcohol.

Tungstates of Silver.—An *acid argentic salt*, $Ag^2O.2WO^3$, or $Ag^2WO^4.WO^3$, is obtained by precipitating acid tungstates of alkali-metal with nitrate of silver, as a white anhydrous salt, insoluble in water, slightly soluble in acetic or phosphoric acids, more easily in ammonia. When ignited, it turns brown, and cakes together to a metallically lustrous mass.—An *acid argentous salt*, $Ag^4O.2WO^3$, is formed, according to Rautenberg, by the action of hydrogen on an ammoniacal solution of the argentic salt. It is a black, glittering, crystalline powder, which is decomposed by nitric acid, leaving tungstic oxide; potash dissolves the tungstic acid, leaving argentous oxide.

Tungstates of Sodium.—The *neutral salt*, Na^2WO^4, or $Na^2O.WO^3$, is prepared like the neutral potassium-salt. It crystallises in transparent, colourless, nacreous, rhombic tables or scales, containing $Na^2WO^4.2H^2O$, having a bitter taste and alkaline reaction, permanent in the air, soluble in 4 pts. of cold and 2 pts. of boiling water, insoluble in alcohol, and precipitated thereby from its aqueous solution. It may be recrystallised without decomposition. When heated to 200°, it gives off all its water, and becomes opaque; and at a temperature somewhat below redness, it melts to a transparent liquid, which solidifies in the crystalline form on cooling. This salt is sometimes used, in place of stannate of sodium, as a mordant in dyeing and calico-printing; also for rendering linen, cotton, &c., uninflammable (see COMBUSTION,

i. 1102). For the methods of preparing it on the large scale, see Richardson and Watts's *Chemical Technology*, i. [4], 48).

Acid salts.—The salt $3Na^2O.7WO^3$, according to Lotz and Scheibler ($5Na^2O.12WO^3$, according to Laurent and Marignac), is prepared similarly to the corresponding potassium-salt—namely, by fusing the neutral salt with a sufficient quantity of tungstic oxide, and boiling the product with water; or by boiling a solution of hydrate, carbonate, or neutral tungstate of sodium with tungstic oxide, and leaving the resulting solution to crystallise; or, again, by fusing wolfram with one-third of its weight of anhydrous carbonate of sodium. It crystallises from cold aqueous solutions with 16 at. water (Scheibler) [28 at. water, according to Marignac's formula], in large striated monoclinic prisms, of specific gravity 3·897 at 14°, sometimes flattened to six-sided tables. It has an astringent and, at the same time, sweet and bitter taste; reddens litmus; dissolves in 2·22 pts. water at 0°, and in 0·24 pt. at 100° (Scheibler); in about 12 pts. of cold water (Marignac). When water at 35°—40° is saturated with this salt, the cooled solution retains 1 pt. of salt dissolved in 9 pts. water; but gradually (in about 7 months), so much separates out that 1 pt. remains dissolved in nearly 12 pts. water. If the salt be boiled for some time with water, a solution is formed, which, when cold, contains, after one to twelve days, 1 pt. salt to 0·68—2·6 pts. water; and after seven months, 1 pt. salt to 9·7 pts. water (Marignac). The salt effloresces in dry air, gives off 12 at. water at 100°, and the rest at 300°, leaving the anhydrous salt, $3Na^2O.7WO^3$, of specific gravity 5·49, and still perfectly soluble in water. It melts at a red heat, and solidifies in the crystalline state on cooling; water then extracts from it the alkaline sesquiacid salt, $2Na^2O.3WO^3$, leaving the anhydrous tetratungstate, $Na^2O.4WO^3$, in the form of a laminar or scaly crystalline mass, having a nacreous lustre. This last-mentioned salt is quite insoluble in water; it does not melt at a moderate heat, but when more strongly heated, cakes together to a semifused mass, containing deep blue-green crystals (? of sodio-tungstous tungstate).

When the solution of the salt, $3Na^2O.7WO^3$, is evaporated by heat, crystals are obtained, containing smaller quantities of water than the above—viz., at 60°—80°, monoclinic crystals containing $3Na^2O.7WO^3.15H^2O$; and at 100°, shining octahedrons, containing $3Na^2.7WO^3.12H^2O$. or $5Na^2O.12WO^3.20H^2O$. (Marignac.)

A salt containing $2Na^2O.5WO^3.12H^2O$, is obtained, according to Forcher, in brilliant translucent crystals, by prolonged digestion of the neutral salt with water, or by saturating a warm solution of that salt with tungstic acid.

A *diacid salt*, $Na^2O.2WO^3.2H^2O$, is precipitated from the solution of the neutral salt by hydrochloric acid, as a crystalline powder (Rammelsberg, Pogg. Ann. xciv. 514).—The *anhydrous diacid salt*, $Na^2O.2WO^3$, or $Na^2WO^4.WO^3$, is formed by fusing 1 at. of the neutral tungstate with 1 at. tungstic acid, and is found in needles lining the cavities of the resulting crystalline mass. (Forcher.)

Ammonio-sodic Tungstates.—*a*. The salt, $\left.\begin{matrix}Na^2O\\2(NH^4)^2O\end{matrix}\right\}7WO^3.3H^2O$, crystallises in white nacreous scales, from a warm concentrated solution of 1 at. neutral sodium-tungstate, mixed with rather more than 1 at. chloride of ammonium.—*β*. $\left.\begin{matrix}3Na^2O\\12(NH^4)^2O\end{matrix}\right\}35WO^3.14H^2O$ separates in crystalline scales, on pouring a boiling solution of 1 at. sodium-tungstate into a boiling solution of 2 at. sal-ammoniac, a large quantity of ammonia being at the same time evolved.—*γ*. The salt $5\left(\begin{matrix}\frac{1}{4}Na^2O\\\frac{3}{4}(NH^4)^2O\end{matrix}\right).12WO^3.12H^2O$, or perhaps, in the pure state, $\left.\begin{matrix}Na^2O\\4(NH^4)^2O\end{matrix}\right\}12H^2WO^4$, crystallises in nacreous rhombic laminæ, on mixing the solutions of the acid tungstates of sodium and ammonium. It is soluble in water, but is resolved by recrystallisation into the ammonium- and sodium-salts.—*δ*. The salt $\left.\begin{matrix}2Na^2O\\3(NH^4)^2O\end{matrix}\right\}12WO^3.5H^2O$, is prepared similarly to the preceding, which it resembles. (Marignac.)

Bario-sodic tungstate has been already described (p. 906).

Potassio-sodic Tungstates.—A mixture of the tungstates of potassium and sodium deposits, first, crystals of the acid potassium-salt, then two double salts, viz., $\left.\begin{matrix}Na^2O\\4K^2O\end{matrix}\right\}.12WO^3.15H^2O$, in monoclinic crystals, and $5\left(\begin{matrix}\frac{3}{11}K^2O\\\frac{8}{11}Na^2O\end{matrix}\right).12WO^3.25H^2O$, in oblique rhombic octahedrons, and lastly, the acid sodium-salt. (Marignac.)

TUNGSTATES OF STRONTIUM.—The *neutral salt*, $SrWO^4$, is prepared like the barium-salt, which it resembles. By fusing 1 pt. of sodium-tungstate with 2 pts. strontium-chloride and 2 pts. common salt, it is obtained in white translucent crystals, having the form of native tungstate of lead. (Schultze.)

The *acid salt* ($SrO.2WO^3.4H^2O$ according to Anthon, $3SrO.7WO^3.4H^2O$ according to Lotz).prepared like the acid barium-salt, is white, insoluble in cold water, decomposed by acids, and becomes anhydrous when heated.

Tungstate of Thorinum.—Thorinum-salts give white flocculent precipitates with the neutral and acid tungstates of alkali-metal.

Tungstate of Tin.—A solution of ammonio-stannic chloride is precipitated by acid ammonium-tungstate, in white flocks, soluble in excess of the tin-salt, also in phosphoric, oxalic, and tartaric acids. (Lotz.)

Tungstate of Tungsten, $W^2O^5 = WO^2.WO^3$.—This is the blue oxide of tungsten, already mentioned as being formed by the reduction of tungstic oxide by zinc and hydrochloric acid, &c. It is likewise produced, as a fine blue powder, when tungstate of ammonium is heated to redness in a retort.

Tungstates of Uranium.—The *uranic salt* is a light-yellow precipitate, insoluble in water, but soluble in the stronger acids, and in ammonia (Berzelius).—An *acid uranous salt*, $2UO.WO^3.6H^2O$, is obtained, by precipitating uranous chloride with an acid tungstate of alkali-metal, as a brownish precipitate, soluble with green colour in hydrochloric acid. (Rammelsberg.)

Tungstate of Vanadium, precipitated by alkaline tungstates from vanadic salts, is brown, somewhat soluble in water, and oxidises in the air with formation of vanadic acid.

Tungstate of Yttrium, $YWO^4.2H^2O$, is a white pulverulent precipitate, slightly soluble in water. (Berlin.)

Tungstate of Zinc, $ZnWO^4$, is obtained, by fusing 1 pt. sodium-tungstate, 2 pts. zinc-chloride, and 2 pts. common salt, and boiling the mass with water, in colourless square prisms, with octahedral faces, probably isomorphous with the calcium-salt. (Geuther and Forsberg.)

Ammonium-zinc-tungstate, $\left.\begin{matrix}2ZnO\\(NH^4)^2O\end{matrix}\right\}7WO^3.3H^2O$, is obtained by precipitating sulphate of zinc with acid tungstate of ammonium, in small snow-white needles, which dissolve sparingly in boiling water, more easily on addition of ammonium-tungstate, zinc-sulphate, oxalic acid, tartaric acid, or phosphoric acid. (Lotz.)

Metatungstic Acid.

Soluble Modification of Tungstic Acid.—This acid is mostly produced in the decomposition of tungstates by the stronger acids at ordinary temperatures; also by the action of tungstic acid on tungstates. Pure metatungstic acid is obtained by decomposing a warm concentrated solution of barium-metatungstate with dilute sulphuric acid; the filtrate, evaporated over oil of vitriol in a vacuum, yields crystals, apparently quadratic octahedrons, of hydrated metatungstic acid, $H^2WO^4.7H^2O$, or $H^2O.WO^3 + 7aq$. (Scheibler), or more correctly, $H^2WO^4.3WO^3.31H^2O$, or $H^2O.4WO^3 + 31aq$. Forcher, by decomposing the lead-salt with sulphydric acid, and leaving the filtrate to evaporate, obtained metatungstic acid in sulphur-yellow crusts, apparently made up of octahedrons.

Metatungstic acid is very soluble in water; the solution has a sour and intensely bitter taste.

A solution	containing	2·79	per cent. WO^3	has a	specific gravity	of 1·0257	at 17·5°.
"	"	12·68	"	"	"	1·1275	
"	"	27·61	"	"	"	1·3274	
"	"	43·75	"	"	"	1·6343	

The solution may be boiled, and evaporated to a syrup over the water-bath, without alteration; but on further concentration by heat, ordinary yellow insoluble tungstic acid separates out suddenly.

Strong *sulphuric acid* added to a concentrated solution of metatungstic acid forms a white precipitate which disappears on addition of water. Aqueous metatungstic acid dissolves *zinc* and *iron*, with evolution of hydrogen, blue oxide of tungsten being formed at the same time.

A *colloïdal* modification of metatungstic acid is obtained by dialysing a 5 per cent. solution of sodium-tungstate mixed with a quantity of hydrochloric acid exactly sufficient to saturate the alkali contained in it. The solution remaining on the dialyser after a few days (amounting to 80 per cent. of the liquid used), has a bitter astringent taste, is not gelatinised by acids or salts even at the boiling heat, and when evaporated to dryness, leaves vitreous scales which adhere strongly to the porcelain dishes. They are colourless if the evaporation has taken place in a vacuum, do not lose their solubility by being heated to 200°, but, at a temperature near redness, are converted into insoluble tungstic oxide, with loss of 2·42 per cent. water. The dry soluble acid is rendered sticky by water, like gum. Its solutions exhibit, at 19°, the following specific gravities:

Quantity of tungstic oxide (WO^3) in 100 pts. .	5	20	50	66·5	79·8.
Specific gravity . . .	1·0475	1·2168	1·8001	2·596	3243.

(Graham, Chem. Soc. J. xvii. 318; Jahresb. 1864, p. 179.)

Metatungstates, $M^2O.4WO^3$, or $M^2WO^4.3WO^3$.—These salts have been examined chiefly by Scheibler (J. pr. Chem. lxxx. 204; Jahresb. 1860, p. 155); but the ammonium-salt, which was the first known, was discovered by Margueritte (Ann. Ch. Phys. [3], xvii. 475). They have the composition of quadracid tungstates, but the tungstic acid obtained from them is not ordinary tungstic acid, but the more soluble modification. They are formed from ordinary tungstates by addition of tungstic acid, or by abstraction of part of the base. The metatungstates of the alkali-metals are best prepared by boiling the solutions of the corresponding tungstates for some time with hydrated tungstic acid, $H^2WO^4.H^2O$, or by dropping an acid (phosphoric acid being the best adapted for the purpose) into the solution of an alkaline tungstate, as long as the tungstic acid separated in the first instance redissolves. The other metatungstates may be prepared from those of the alkali-metals by double decomposition, and very easily by decomposing the metatungstate of barium with soluble sulphates. The metatungstates may also be prepared by the direct combination of metatungstic acid with bases, or by its action on carbonates, nitrates, or chlorides, all of which it decomposes.

The metatungstates are for the most part soluble and crystallisable; some are very soluble, and leave amorphous gummy masses when evaporated; according to Marignac, they react nearly neutral, colouring litmus violet; they effloresce in dry air, and give off the greater part of their crystallisation-water below 100°. The metatungstates of the alkali-metals do not melt at a red heat, but merely bake together, decomposing at the same time, with formation of blue oxide. Their solutions do not precipitate the salts of the earth-metals, or of the heavy metals, excepting those of *lead* and *mercurosum*. They give no precipitate with *ferrocyanide of potassium*.—*Acids* added to the solutions of metatungstates do not precipitate either white or yellow tungstic acid.—*Zinc* and *hydrochloric acid* colour them blue, changing to reddish-violet (not to brown like the ordinary tungstates: Forcher). These reactions are sufficient to distinguish the metatungstates from the acid tungstates, with which they are in some cases isomeric. They are, however, easily reconverted into ordinary tungstates by addition of aqueous alkalis, the solutions being then precipitated by acids, as well as by the salts of the alkaline earth-metals and other metals.

Metatungstic acid precipitates the solutions of *organic bases* in flocks, and may therefore be used as a reagent for these bases; the solution of a metatungstate acidulated with a mineral acid, or ordinary tungstate of sodium mixed with excess of phosphoric acid, may be used for the purpose. This reaction with metatungstic acid is said to be even more delicate than that with phospho-molybdic acid, a distinct turbidity being produced by metatungstic acid in a solution containing not more than 1 pt. in 200,000 of quinine or strychnine.

Metatungstate of Ammonium, $(NH^4)^2W^4O^{13}.8H^2O$, or $(NH^4)^2O.4WO^3 + 8aq.$ according to Scheibler; $2(NH^4)^2W^4O^{13}.15H^2O$, according to Lotz.—This salt, discovered by Margueritte, is produced by boiling tungstate of ammonium, either alone, whereupon ammonia is given off, or with tungstic acid, which is dissolved. On evaporating the solution to a syrup, ordinary ammonium-tungstate separates out first, and the filtrate deposits the metatungstate in highly lustrous transparent octahedrons, which effloresce on exposure to the air. The salt is very soluble in water, melting at first at the bottom of the liquid, like phosphorus. The solution is strongly refractive, is not precipitated by hydrochloric or nitric acid, but when mixed with ammonia, and evaporated, yields crystals of ordinary acid tungstate, $3(NH^4)^2O.7WO^3$ (Lotz).—From the mother-liquor of the octahedral metatungstate just described, Margueritte obtained the salt $(NH^4)^2O.6WO^3 + 13aq.$, in well-defined crystalline laminæ. — The *potassium-salt*, $K^2W^4O^{13}.8H^2O$, obtained by boiling the tungstate with tungstic acid, crystallises in shining octahedrons resembling the ammonium-salt. The same solution yields slender needle-shaped crystals, which, however, are converted into the octahedral salt by recrystallisation; the salt appears therefore to be dimorphous (Scheibler).—The *sodium-salt*, $Na^2W^4O^{13}.10H^2O$, also crystallises in shining octahedrons, apparently regular, of specific gravity 3·84, and very efflorescent. One part of water at ordinary temperatures dissolves 10·69 pts. of these crystals, forming a solution of specific gravity 3·019; hot water dissolves the salt in all proportions. The salt gives off all its water at a heat much below redness, and if it has not been too strongly heated, still dissolves completely, though slowly, in water (Marignac). In other respects it behaves like the potassium- and ammonium-salts. Margueritte likewise mentions a salt containing $Na^2W^4O^{13}.4H^2O$.—The *lithium-salt* dries up over oil of vitriol to an amorphous mass.

Metatungstate of Barium, $BaW^4O^{13}.9H^2O$, is obtained by mixing the warm concentrated solutions of ammonium-metatungstate and barium-chloride, and, when purified by recrystallisation, forms large, shining, quadratic octahedrons, modified by the prismatic faces and the perpendicular end-faces. They have a specific gravity of 4·298, effloresce in the air, and give off 6 at. water at 100°; at a red heat the salt becomes yellow and insoluble. The crystals are decomposed by cold water into the insoluble triacid salt, $BaW^3O^{10}.6H^2O$, and free tungstic acid, which, however, recombine at the boiling heat. The metatungstate dissolves easily in boiling water; the solution yields metatungstic acid when decomposed by dilute sulphuric acid, and the other metatungstates (as those of magnesium, zinc, cadmium, cobalt, nickel, &c.), by double decomposition with soluble sulphates.—The *strontium-salt*, $SrW^4O^{13}.8H^2O$, obtained like the barium-salt, crystallises in quadratic octahedrons, modified by the faces oP and ∞P∞.—The *calcium-salt*, formed by decomposing chloride or carbonate of calcium with metatungstic acid, crystallises with difficulty.—The *magnesium-salt*, $MgW^4O^{13}.8H^2O$, forms shining, probably monoclinic crystals, permanent in the air.—The *glucinum-salt* is very soluble, but crystallises from a syrupy solution, in delicate deliquescent laminæ.—The *aluminium-salt* dries up to an amorphous mass.

Metatungstate of Cadmium, $CdW^4O^{13}.10H^2O$, forms shining quadratic octahedrons, permanent in the air.—The *cerous salt*, $CeW^4O^{13}.10H^2O$, prepared by decomposing cerous carbonate with metatungstic acid, crystallises in pale, lemon-yellow, monoclinic crystals, permanent in the air.—The *lanthanum-* and *didymium-salts* are also crystallisable.—The *cobalt-salt*, $CoW^4O^{13}.9H^2O$, crystallises in quadratic octahedrons; the *cupric salt*, $CuW^4O^{13}.11H^2O$, in laminæ and tables, probably belonging to the monoclinic system.—The *ferric salt* dries up to an amorphous mass; its solution, mixed with ammonia, yields a precipitate of ferric tungstate, while ammonio-ferric tungstate remains in solution.—The *ferrous salt*, prepared by dissolving iron in metatungstic acid, is crystallisable, but difficult to obtain pure. The solution, which has a fine blue colour, contains blue oxide of tungsten, as well as the ferrous salt.—The *lead-salt*, $PbW^4O^{13}.6H^2O$ (Lotz), or $PbW^4O^{13}.5H^2O$ (Scheibler), is obtained by precipitating a moderately concentrated solution of the acid, or the ammonium-salt, with acetate of lead, as a white flocculent salt, which dissolves in a large quantity of hot water, and crystallises by slow evaporation in slender silky needles, easily soluble in nitric acid.—The *manganous salt*, $MnW^4O^{13}.10H^2O$, forms beautiful, light-yellow, quadratic octahedrons, with perpendicularly truncated summits; they are permanent in the air.—The *mercurous salt*, $Hg^2W^4O^{13}.25H^2O$ (?), is obtained on adding mercurous nitrate to the free acid, or an alkaline metatungstate, as a white bulky precipitate, which shrinks considerably in drying, and assumes a lemon-yellow colour.—The *nickel-salt*, $NiW^4O^{13}.8H^2O$, forms monoclinic prisms and tables.—The *silver-salt*, $Ag^2W^4O^{13}.3H^2O$, is best prepared by mixing the boiling solutions of equivalent quantities of sodium-metatungstate and silver-nitrate, with addition of a few drops of nitric acid; the clear solution, on cooling, deposits the salt in waxy crusts, consisting of microscopic octahedrons. It dissolves easily in water, crystallises by evaporation over oil of vitriol, but remains as an amorphous mass when the solution is evaporated by heat.—The *zinc-salt*, $ZnW^4O^{13}.10H^2O$, is very soluble, and crystallises with difficulty.

Ethylic Metatungstate, probably $(C^2H^5)^2W^4O^{13}.3H^2O$, is produced by heating the silver-salt with ethylic iodide in sealed tubes, and remains, on distilling off the free ethylic iodide, exhausting with absolute alcohol, and evaporating quickly in a vacuum, as a thick viscid syrup, which slowly dries up, over oil of vitriol, to a greenish fissured mass. It is very unstable, and is instantly decomposed by water, yielding tungstic hydrate.

Ordinary tungstate of silver, heated with ethylic iodide, does not yield a tungstic ether.

TUNGSTEN, OXYBROMIDES OF. (See p. 899.)

TUNGSTEN, OXYCHLORIDES OF. (See p. 900.)

TUNGSTEN, PHOSPHIDES OF. Phosphorus and tungsten combine directly, but without incandescence, when finely-pulverised metallic tungsten is heated to redness in phosphorus-vapour. The resulting compound is a dull dark-grey powder, very difficult to oxidise, and containing W^3P^4.—Another compound, W^4P^2, is obtained in beautiful crystalline groups, like natural geodes, by reducing a mixture of 2 at. phosphoric and 1 at. tungstic anhydride, at a very high temperature, in a crucible lined with charcoal. The crystals are six-sided prisms, sometimes an inch long, having a steel-grey colour and strong lustre; specific gravity = 5·207. This compound is a good conductor of electricity, is scarcely oxidised when heated to redness, but burns with great splendour on charcoal in a stream of oxygen, or on fused chlorate of potassium; it is not attacked by any acid, not even by nitromuriatic acid. (Wöhler, Chem. Soc. J. v. 94.)

TUNGSTEN, SULPHIDES OF. The *disulphide*, WS^2, is formed when tungsten, or one of its oxides, is heated to redness with sulphur, or certain volatile sulphur-compounds. It is prepared by igniting tungsten or tungstic oxide with 6 pts. of cinnabar, or by passing the vapour of carbonic disulphide or sulphydric acid over tungstic oxide heated to redness in a porcelain tube; also by igniting the trisulphide in a close vessel (Berzelius and Borck). Riche prepares it by fusing equal parts of acid potassium-tungstate and sulphur in a crucible, and lixiviating the mass with water.

Disulphide of tungsten is (according to Berzelius) a greyish-white powder, acquiring, by pressure, a steel-grey colour and metallic lustre. According to Riche, it forms slender, soft, black, needle-shaped crystals, which soil the fingers like graphite. It is oxidised by ignition in the air, or in vapour of water, also when gently heated with nitric or nitromuriatic acid. It is not altered by fusion with cyanide of potassium. (Wöhler and v. Uslar.)

The *trisulphide*, or *Tungstic Sulphide*, WS^3, has hitherto been obtained only in the wet way. It is prepared by dissolving tungstic oxide in sulphydrate of ammonium or potassium, and precipitating with an acid; or by saturating an aqueous solution of alkaline tungstate with sulphydric acid, and precipitating with hydrochloric acid. It is black when dry, and yields a liver-coloured powder; dissolves slightly in cold water, more easily in boiling water; and is precipitated almost completely by sal-ammoniac and other salts, and by acids. When boiled with hydrochloric acid, the precipitate becomes denser and darker-coloured, ultimately black-blue, but remains soluble in water. It dissolves easily, especially when recently precipitated, in hydrate or carbonate of potassium, and in ammonia. When ignited, alone or with cyanide of potassium, it is reduced to the disulphide.

Trisulphide of tungsten unites readily with basic metallic sulphides, forming sulphur-salts called sulphotungstates, represented for the most part by the formula M^2WS^4, or $M^2S.WS^3$, analogous to that of the neutral tungstates. The sulphotungstates of the alkali-metals and alkaline earth-metals may be prepared by dissolving the trisulphide in the corresponding sulphydrates, or by treating the corresponding tungstates with sulphydric acid When trisulphide of tungsten is dissolved in a caustic alkali or an alkaline carbonate, a tungstate is formed, together with the sulphotungstate; and the resulting solution yields, with acids, a light red-brown precipitate of tungstic oxysulphide, which does not turn black when boiled with hydrochloric acid. The insoluble sulphotungstates of the earth-metals, and heavy metals, are obtained by precipitation, or by boiling a solution of alkaline sulphotungstate with the corresponding oxides.

The *ammonium-salt*, $(NH^4)^2WS^4$, separates from a concentrated solution in yellowish-red crystals; and the mother-liquor, when left to evaporate, deposits yellow rectangular tables. The salt is somewhat sparingly soluble; it decrepitates when heated, and when ignited out of contact of air, leaves tungstic sulphide in lumps having a metallic lustre.

The *potassium-salt*, K^2WS^4, separates from its aqueous solution, on evaporation, in anhydrous yellow crystals, or smooth, pale, four-sided red prisms, with dihedral summits, and is precipitated by alcohol in delicate cinnabar-red prisms. The aqueous solution, mixed with a small quantity of hydrochloric acid, yields, by evaporation, a black mass, consisting of an acid sulphotungstate, $K^2S.2WS^3$, or $K^2WS^4.WS^3$.—The aqueous solution of the neutral salt, boiled with cupric hydrate, yields cupric sulphide and tungstate of potassium. If the solution of the sulphotungstate contains also tungstate of potassium, or if the tungstate be fused with sulphur and the fused mass dissolved in water, the solution yields by evaporation lemon-yellow rectangular plates of the *oxysulphotungstate*, $K^2WS^2O^2.2H^2O$. A solution of 2 pts. potassium-sulphotungstate and 1 pt. potassium-nitrate, yields ruby-red transparent crystals of a double salt, containing $K^2WS^4.KNO^3$, which detonates like gunpowder when heated to commencing redness, yielding a pale-yellow mass, from which water extracts tungstate and sulphotungstate of potassium, leaving disulphide of tungsten.

The *sodium-salt*, Na^2WS^4, crystallises with difficulty from the aqueous, more easily from the alcoholic solution, by spontaneous evaporation. The crystals, when exposed to the air, soon become moist and yellow. There is also an acid salt, soluble in water and in alcohol.

The *barium-salt* is prepared by passing sulphydric acid gas through water in which tungstate of barium is suspended, and crystallises by evaporation in yellow, transparent, crystalline crusts. When tungstic sulphide is dissolved to saturation in protosulphide of barium, the yellow solution yields, by evaporation, a brown amorphous mass.—The *calcium-salt*, prepared like the barium-salt, is an amorphous mass, easily soluble in water and in alcohol; the *strontium-* and *magnesium-salts*, prepared in like manner, are also soluble in water and in alcohol; the former separates in lemon-yellow radiate crystals, the latter is uncrystallisable. The solutions of the calcium-, strontium-, and magnesium-salts take up an additional quantity of tungstic sulphide, and then leave, on evaporation, brown or brown-red amorphous masses.—The *manganous salt*, $Mn''WS^4$, also dissolves in water, forming a yellow solution.

The *cadmium-salt*, $Cd''WS^4$, and the *zinc-salt* are yellow precipitates, the latter separating gradually; the *cerium-salt* is also a yellow precipitate, which separates only after 24 hours.—The sulphotungstates of *cobalt*, *copper*, *lead*, and *nickel*, represented by the general formula $M''WS^4$, are brown or black-brown precipitates.—The *mercuric salt*, $Hg''NS^4$, is precipitated, on mixing the solutions of mercuric chloride and potassium-sulphotungstate in equivalent proportions, in orange-yellow flocks; with an excess of mercuric chloride, the precipitate is white; with an excess of the alkaline sulphotungstate, black.—The *mercurous salt*, Hg^2WS^4, is a black precipitate; the *silver-salt*, Ag^2WS^4, dark-brown.—The *stannous salt*, $Sn''WS^4$, is precipitated in brown flocks; the *stannic salt*, $Sn^{iv}(WS^4)^2.Sn^{iv}S^2$, in greyish-yellow flocks.—The *platinic salt*, $Pt^{iv}(WS^4)^2$, and the *auric salt*, $Au'''(WS^4)^3$, are black precipitates; the *bismuth-salt*, $Bi'''(WS^4)^3$, dark-brown, nearly black.—The *ferric salt*, $Fe'''(WS^4)^3$, is a dark-brown bulky precipitate. Ferrous salts do not precipitate a solution of potassium-sulphotungstate. (Berzelius.)

TUNGSTEN-METHYL. $W(CH^3)^4$. (Riche, Compt. rend. xlii. 203.—Cahours, Jahresb. 1861, p. 353.)—When tungsten is heated with methylic iodide to 240° in a sealed tube for several days, a viscid liquid is formed, from which ether-alcohol extracts iodide of tungsten-methyl, consisting, according to Riche, of $W(CH^3)^4I^2$, but, according to Cahours's analysis, of $W^{vi}\left\{\begin{matrix}(CH^3)^4\\ I^2\end{matrix}\right.$, a composition which is in accordance with the known atomicity of tungsten. This iodide crystallises in colourless tables, melts at 110°, and when agitated with recently-precipitated silver-oxide, is converted into oxide of tungsten-methyl, or tungstic oxytetramethide, $W^{vi}\left\{\begin{matrix}(CH^3)^4\\ O''\end{matrix}\right.$. This oxide dissolves in acids, forming uncrystallisable salts, remaining, when concentrated, as viscid liquids, from which the oxide is reprecipitated by alkalis.

Tungsten heated, in like manner, with *ethylic iodide* is scarcely attacked, only a few needles of tungstic oxyiodide being formed, which float about in the liquid. (Riche.)

TUNGSTIC COMPOUNDS. Compounds in which tungsten is hexatomic, viz., WCl^6, WO^3, $W(CH^3)^4I^2$, &c.

TUNGSTOSILICIC ACIDS. (Marignac, Ann. Ch. Phys. [4], iii. 5; Jahresb. 1864, p. 220.)—These are tetrabasic acids, containing both silicon and tungsten. Their names and formulæ, as given by Marignac, are as follows:

Silicoduodecitungstic or Silicotungstic acid . . .	$4H^2O.SiO^2.12WO^3$.
Tungstosilicic acid	$4H^2O.12WO^3.SiO^2$.
Silicodecitungstic acid	$4H^2O.SiO^2.10WO^3$.

They may be regarded as tungstates of silicon and hydrogen, the first two having the composition $H^8Si^{iv}O^6.12WO^3$, which is referable to that of an acid tungstate, $M^2O.2WO^3$.

The potassium- or sodium-salt of the first of these acids is produced by boiling gelatinous silica with acid tungstate of potassium or sodium, its formation probably taking place as represented by the equation:

$$\left.\begin{matrix}6(K^2O.2WO^3)\\ \text{or } K^{12}O^6.12WO^3\end{matrix}\right\} + Si(HO)^4 = K^8Si^{iv}O^6.12WO^3 + 4K(HO).$$

The resulting solution yields, with mercurous nitrate, a precipitate of mercurous silicotungstate; this, when decomposed by an exactly equivalent quantity of hydochloric acid, yields a solution of hydric silicotungstate, or silicotungstic acid; and the other silicotungstates, which are all soluble, are obtained by treating the acid with carbonates.

Silicodecitungstic acid is obtained as an ammonium-salt by boiling gelatinous silica with solution of acid tungstate of ammonium; and from this, the acid and its other salts may be obtained in the same manner as the preceding. The silicodecitungstates are very unstable, and the acid is decomposed by mere evaporation, depositing silica, and being converted into tungstosilicic acid, which is isomeric with silicotungstic acid, and likewise decomposes carbonates. All three of these acids are capable of exchanging either one half or the whole of their basic hydrogen for metals, thereby forming acid and neutral salts; silicotungstic acid also forms an acid sodium-salt, in which only one-fourth of the hydrogen is replaced by sodium.

Silicotungstic Acid, $4H^2O.SiO^2.12WO^3 = H^8SiW^{12}O^{42}$.—The concentrated solution of this acid, obtained as above, yields the acid, by spontaneous evaporation, in large, shining, colourless (or slightly yellowish), quadratic octahedrons, containing $H^8SiW^{12}O^{42} . 29H^2O$. They are combinations of P . ∞P∞ . oP, having the angle P : P in the terminal edges = 109° 9′; in the lateral edges = 110° 6′. They effloresce in contact with the air, begin to melt at 36°, and fuse completely, at 53°, to a liquid which yields another crystalline hydrate. At 100° they give off 25 at. water, another portion at a higher temperature, and the remainder at 350°; at this temperature, however, the acid retains its solubility; but at a stronger heat, it is converted into an insoluble mixture of silicic and tungstic anhydrides. The other hydrate, above mentioned as separating from the melted acid, contains $H^8SiW^{12}O^{42} . 22H^2O$, and is likewise formed when the acid separates from a solution containing hydrochloric or sulphuric acid. The crystals are combinations of a rhombohedron (R) with the basal end-face and a subordinate acute rhombohedron, whereby they acquire the character of cubo-octahedrons (R : R in the terminal edges = 88° 48′; oP : R = 124° 25′); they are distinguished from the octahedral crystals by their permanence in the air. Silicotungstic acid dissolves easily in water and in alcohol; the aqueous solution, saturated at 18°, contains 1 pt. of the octahedral acid to 0·104 pt. water, and has a density of 2·283. The alcoholic solution mixes with an equal volume of ether without turbidity; but, on adding more ether, the concentrated ethereal solution separates as a syrupy layer, which forms a clear solution in water, but becomes turbid and gives up the ether when heated. The same syrupy liquid (which does not contain any silicotungstic ethers), is obtained by exposing either the octahedral or the rhombohedral crystals to ether-vapour.

Silicotungstates.—Silicotungstic acid is a strong acid, decomposing carbonates, and easily forming double salts. The salts are all soluble in water, excepting the mercurous salt, and almost all crystallise well. They are not altered by boiling with hydrochloric acid. Caustic alkalis and alkaline carbonates throw down silicic acid from their solutions; the precipitate formed by ammonia redissolves at the boiling heat. When heated to redness, they glow slightly, and leave a residue containing free tungstic anhydride.

Silicotungstate of Aluminium is obtained by dissolving aluminium-hydrate in silicotungstic acid, or by adding the latter to a solution of aluminium-chloride, in large regular octahedrons containing $\overset{\prime\prime}{Al}{}^4H^{12}Si^3W^{36}O^{126}.87H^2O$, or $2Al^2O^3.6H^2O.3(SiO^2.12WO^3) . 87aq$. The cold solution is rendered turbid by addition of ammonia, but becomes clear again when warmed, and yields, after evaporation of the excess of ammonia, an octahedral double salt, containing $2Al^2O^3.9(NH^4)^2O.3(SiO^2.12WO^3) . 75aq$.

Ammonium-salts.—The *octammonic* or *tetrabasic salt*, $(NH^4)^8SiW^{12}O^{42}.16H^2O = 4(NH^4)^2O.SiO^2.12WO^3.16aq.$, is produced by saturating the acid with ammonia, or by prolonged boiling of a solution of silicodecitungstate of ammonium, and remains, on leaving the solution to evaporate, in opaque white nodules. By boiling with hydrochloric acid, it is converted into the *tetrammonic salt*, $(NH^4)^4H^4SiW^{12}O^{42}.6H^2O$. Both these salts, when heated with ammonia, yield sparingly soluble acid tungstate of ammonium, which separates, and silicodecitungstate of ammonium, which crystallises on evaporation.

Barium-salts.—On mixing a solution of silicotungstic acid with carbonate of barium till a permanent precipitate of neutral salt is produced, the clear liquid yields, on evaporation, monoclinic prisms of the *dibarytic salt*, $\overset{\prime\prime}{Ba}{}^2H^4SiW^{12}O^{42}.14H^2O$, which, by prolonged contact with the mother-liquor, are converted into a more highly hydrated efflorescent salt, containing $\overset{\prime\prime}{Ba}{}^2H^4SiW^{12}O^{42}.14H^2O$. On adding chloride of barium to an excess of a hot solution of sodium-silicotungstate, a double salt, $\overset{\prime\prime}{Ba}{}^3Na^2SiW^{12}O^{42}.28H^2O$, separates, on cooling, in crystals apparently having the form of rhombic octahedrons. They are decomposed by continued washing, leaving a pulverulent, nearly insoluble tetrabasic salt.

Calcium-salts.—The *dicalcic* or *acid salt*, $\overset{\prime\prime}{Ca}{}^2H^4SiW^{12}O^{42}.22H^2O$, crystallises from a syrupy solution in very large, shining, rhombohedral crystals, R . oP, permanent in the air. The warm solution takes up carbonate of calcium, but the resulting neutral salt is not crystallisable.

Magnesium-salts.—The *acid salt*, $\overset{\prime\prime}{Mg}{}^2H^4SiW^{12}O^{42}.16H^2O$, forms triclinic prisms, permanent in the air.—The *neutral salt* is not crystallisable.

The *mercurous salt*, $Hg^8SiW^{12}O^{42}$, is a heavy yellow precipitate, insoluble in water, very slightly soluble in dilute nitric acid.

Potassium-salts.—*a.* The *neutral salt*, $K^8SiW^{12}O^{42}.14H^2O$, prepared by boiling gelatinous silica with acid potassium-tungstate, crystallises, on cooling from the hot filtered solution, in hard granular crusts, which may be purified by recrystallisation; the crystals look like cubes, but exhibit double refraction. The salt dissolves in 10 pts. water at 18°, and in less than 3 pts. boiling water.—β. The *tetrapotassic salt*, $K^4H^4SiW^{12}O^{42} . 16H^2O$, crystallises, on evaporating a solution of the neutral salt mixed with hydrochloric acid, in large, colourless, shining, hexagonal prisms, with pyramidal summits, $\infty P . P$. Angle $P : P$, terminal = 144° 46'; lateral = 74° 30; prismatic faces longitudinally striated. The crystals effloresce slightly in the air, and at 100° give off their water of crystallisation, together with 1 at. of the basic water. They dissolve in 3 pts. water at 20°.—γ. A solution of the tetrapotassic salt mixed with hydrochloric acid, then evaporated and left to cool, deposits, first a pulverulent very acid salt, then crystals of the tetrapotassic salt; but when these two salts are left for some time in the mother-liquor, they both disappear, and another salt is deposited in monoclinic prisms containing $2K^3H^5SiW^{12}O^{42} . 25H^2O^2$; they are decomposed by solution in water, the liquid, when evaporated, yielding, first crystals of rhombohedral silicotungstic acid, then the salt β, and lastly the salt γ.

The *silver-salt*, $Ag^4H^4SiW^{12}O^{42} . 7H^2O$, separates as a crystalline precipitate when carbonate of silver is dissolved in silicotungstic acid, or when this acid is added to a solution of silver-nitrate. It is slightly soluble in water, easily soluble in dilute nitric acid.

Sodium-salts.—α. The *neutral salt*, $Na^8SiW^{12}O^{42} . 7H^2O$, is prepared like the neutral potassium-salt, and crystallises by spontaneous evaporation in slender needle-shaped crystals. The saturated solution contains 0·21 pts. water to 1 pt. of the salt, and has a specific gravity of 3·05 at 19°.—β. The *tetrasodic salt*, $Na^4H^4SiW^{12}O^{42}$, crystallises from a solution of the neutral salt mixed with hydrochloric acid, with amounts of water varying according to circumstances. If the crystallisation takes place at 40°—50°, or from a solution containing hydrochloric acid, at ordinary temperatures, triclinic tabular crystals are obtained, containing 11 at. water. A pure, concentrated, aqueous solution deposits, at ordinary temperatures, nacreous, efflorescent, triclinic prisms with 18 at. water. A hot concentrated solution deposits, on cooling, first crystals of the 11-hydrated salt, afterwards triclinic prisms differently modified and containing a different amount of water, and finally the 18-hydrated salt. When nitric acid is used, in place of hydrochloric acid, in the preparation of the tetrasodic salt, the mother-liquor yields on concentration a double salt, $4NaNO^3.3(Na^4H^4SiW^{12}O^{42}. 13H^2O)$, in hygroscopic triclinic prisms, mostly twins with the combination-face $\infty\breve{P}\infty$. —γ. The *disodic salt*, $Na^2H^6SiW^{12}O^{42}.14H^2O$, crystallises, on evaporating a solution of the tetrasodic salt, mixed with sulphuric or silicotungstic acid, in triclinic tabular crystals, very much like those of the tetrasodic salt deposited from a warm solution. This salt decomposes when dissolved in water.

Tungstosilicic Acid, $H^8W^{12}SiO^{42} = 4H^2O.12WO^3.SiO^2$ (Marignac).—This acid, isomeric with silicotungstic acid, is produced when a solution of silicodecitungstic acid is evaporated to dryness by heat, and crystallises from a solution filtered from silica, and evaporated to a syrup, in triclinic prisms, exhibiting the dominant combination $\infty{}'P . \infty P'_{,} . \infty\breve{P}\infty . oP$, with domes and hemipyramids subordinate. The crystals deliquesce in damp air. They melt below 100° in their water of crystallisation, and then dry up with intumescence. At 200°, the residue crumbles to a fine powder, which contains 2 at. water, and redissolves in water, with rise of temperature; the acid does not lose its solubility even when heated above 300°. It is also easily soluble in alcohol, and behaves to ether like silicotungstic acid (p. 915).

The tungstosilicates are obtained by saturating the acid with carbonates. Some of them are uncrystallisable, and others are distinguished from the corresponding silicotungstates by their crystalline form, degree of solubility, and amount of water of crystallisation; but there is no characteristic reaction by which the two isomeric acids can be distinguished one from the other.

Tungstosilicate of aluminium, $2Al^2O^3.6H^2O.3(12WO^3.SiO^2).75H^2O$, crystallises from a syrupy solution of gelatinous alumina in tungstosilicic acid, in triclinic prisms, resembling the calcium-salt, and frequently united in twins by the face $\infty{}'_{,}P$.

The *ammonium-salt* has not been obtained of definite composition.

Barium-salt.—On saturating a solution of tungstosilicic acid with baryta-water, a precipitate is formed, which redissolves in the acid liquid on stirring, until more than 2 at. baryta have been added, after which it unites into a layer, oily when warm, resinous in the cold, and drying up in contact with the air to a vitreous mass, consisting of the neutral barium-salt, $Ba^4SiW^{12}O^{42} . 9H^2O$, or $4BaO.12WO^3.SiO^2 . 9aq$. It becomes glutinous again in contact with water, and after prolonged contact crumbles to a powder, which in the air-dried state contains $4BaO.12WO^3.SiO^2 . 27aq$.

The *acid calcium-salt*, $2CaO.2H^2O.12WO^3.SiO^2 . 20aq.$, forms triclinic crystals, $\infty{}'_{,}P . \infty P'_{,} . \infty\breve{P}\infty . oP$ &c., tabular from predominance of $\infty\breve{P}\infty$; it is hygroscopic in moist air. Sometimes another salt, $5CaO.3H^2O.2(12WO^3.SiO^2).47aq.$, was obtained in small shining triclinic crystals, less hygroscopic than the former.

Potassium-salts.—The *neutral salt*, $4K^2O.12WO^3.SiO^2.20aq.$, forms small ill-defined prismatic crystals belonging to the trimetric system.—The *tetrapotassic acid salt*, $2K^2O.2H^2O.12WO^3.SiO^2.7aq.$, likewise crystallises in the trimetric system, and in short hard prisms. $\infty P . \bar{P}\infty . oP$, having the angle $\infty P : \infty P = 101° 0'$; $\infty P . \bar{P}\infty = 131° 0'$; $\bar{P}\infty : \bar{P}\infty$ (basal) $= 116° 28'$; or in friable, nacreous, six-sided tables, arranged in radiate groups.

Sodium-salts.—The *acid salt*, $2Na^2O.2H^2O.12WO^3.SiO^2.10aq.$, forms large rhombohedrons, $R - \frac{1}{2}R$, having the terminal angle $R : R = 87° 0'$.—The *neutral salt* was not obtained in the crystalline form.

Silicodecitungstic acid, $H^8SiW^{10}O^{36}$, $= 4H^2O.SiO^2.10WO^3$, is obtained by heating gelatinous silica with acid tungstate of ammonium, precipitating with mercurous nitrate, or better with silver-nitrate, in the cold, and decomposing the precipitate, after thorough washing, with hydrochloric acid, carefully avoiding an excess. On evaporating the filtered solution in a vacuum, at ordinary temperatures, the acid remains as a transparent yellow glass, containing $H^4SiW^{10}O^{36}.3H^2O$. On exposure to the air, it rapidly absorbs water, splits into fragments, and finally deliquesces. With alcohol and ether, it behaves like silicotungstic acid. The aqueous solution may sometimes be repeatedly evaporated without alteration, but, in most cases, it easily splits up into gelatinous silica and tungstosilicic acid. It does not precipitate the salts of calcium, magnesium, lead, or aluminium; with *nitrate of silver*, it forms a heavy yellowish precipitate, easily soluble in dilute nitric acid; with *mercurous nitrate* a white precipitate, slightly soluble in nitric acid.

Most of the silicodecitungstates are difficult to obtain in the pure state, on account of their great solubility.—The *ammonium-salt* contains $(NH^4)^8SiW^{10}O^{36}.8H^2O$.—The *neutral potassium-salt* appears to crystallise with 17 at. water; the *acid salt*, $K^4H^4SiW^{10}O^{36}$, with 8 at. and 10 at. water; an *ammonio-potassic salt*, $K^4(NH^4)^3HSiW^{10}15H^2O$, was likewise obtained.—The *barium-salt*, $Ba^4SiW^{10}O^{36}$, is obtained, by adding the acid to an excess of barium-chloride solution, as a viscid insoluble precipitate, which, when dried in the air, contains 22 at. water.—The *silver-salt*, dried at 100°, contains $Ag^8SiW^{10}O^{36}.3H^2O$.

TUNGSTOSO-TUNGSTIC COMPOUNDS. Compounds intermediate in composition between tungstous and tungstic compounds: *e.g.*, $W^2Cl^{10} = WCl^4.WCl^6$; $WO^5 = WO^2.WO^3$.

TUNGSTOUS COMPOUNDS. Compounds in which tungsten is quadri-equivalent: *e.g.*, WCl^4, WO^2, WS^2, &c.

TUNICIN. A substance isomeric, and perhaps identical, with cellulose, $(C^6H^{10}O^5)$, occurring in the mantle of Ascidia, and separated therefrom (from the mantle of Cynthia, for example) by successive treatment with water, alcohol, ether, acids, and alkalis. It then remains as a colourless mass, exhibiting the structure of the original substance (Schmidt, Ann. Ch. Pharm. liv. 318).—Berthelot (Compt. rend. xlvii. 227) boils the mantles, first with strong hydrochloric acid, then with potash-ley of specific gravity 1·28, and washes the residue thoroughly with distilled water.

Tunicin exhibits most of the characteristic properties of cellulose, and its insolubility in various liquids; but it is more stable, not being altered by nitric, hydrochloric, or acetic acid, or strong potash-solution, even after prolonged boiling; neither is it blackened by fluoride of boron. In fuming nitric or sulphuric acid, it deliquesces to a colourless liquid; and if the liquid obtained with sulphuric acid be boiled for some time with water, the resulting solution will be found to contain glucose, or a similar sugar.

TURBETH. Syn. with TURPETH.

TURGITE. A name applied by Hermann to a massive variety of brown hæmatite, $2Fe^2O^3.H^2O$, occurring near the River Turga, in the Ural; it appears to be identical with Breithaupt's *hydrohæmatite* from Siebenhitz, near Hof, in Bavaria. (Handw. d. Chem. viii. 1043.)

TURMALINE. Syn. with TOURMALINE (p. 875).

TURMERIC. *Curcuma. Radix Curcumæ. Terra merita.*—The root of *Amomum Curcuma*, a plant cultivated in India and Java. It contains, according to Pelletier and Vogel, a strong-smelling volatile oil, gum, a yellow colouring-matter (*curcumin*), a brown colouring-matter, starch, cellulose, and a small quantity of calcium-chloride. It is used for dyeing wool and silk; but the colour, though a fine yellow, is not durable. It is also employed in pharmacy for colouring certain ointments, and (especially in India) as an ingredient of curry-powder and other condiments.—Alcoholic tincture of turmeric, or paper stained with the aqueous or alcoholic solution, is used as a test for alkalis, and for boric acid (i. 639).

The root of *Canna speciosa*, a plant of frequent occurrence in West Africa, is said to be exactly similar to East Indian turmeric-root, in taste, smell, and chemical reactions (Daniell, Pharm. J. Trans. xix. 258.)

TURNBULL'S BLUE. Ferrous ferricyanide, prepared by precipitating a ferrous salt with ferricyanide of potassium. (See CYANIDES OF IRON, ii. 244.)

TURNERITE. A silicate of aluminium, iron (ferricum), calcium, and magnesium, occurring at Mont Sorel in Dauphiné, and at Tavetsch, in yellow monoclinic crystals, having an adamantine lustre and conchoïdal fracture. Axes $a : b : c = 1 : 0{\cdot}921696 : 0{\cdot}95844$. Angle $b : c = 102° 42'$; $\infty P : +P = 141° 23'$; $+P : +P\infty = 143° 44'$; $\infty P : \infty P\infty = 131° 58'$. In the mineral from Tavetsch, the combination $\infty P . \infty P\frac{1}{3} . \infty P2 . \infty P\infty . oP . +P\infty . [\frac{1}{3}P\infty] . [\frac{1}{4}P\infty] . [P\infty] . P . 2P2 . +\frac{1}{3}P . +\frac{1}{2}P . -\frac{1}{3}P$ was observed. In that from Dauphiné, the faces $-P\infty$ and $[2P\infty]$ likewise occur. (G. v. Rath, Jahresb. 1863, p. 824.)

TURNER'S YELLOW: also called *Patent Yellow*. Oxychloride of lead, $Pb^4Cl^2O^3$. (iii. 545).

TURNIP. See BRASSICA (i. 654).

TURPENTINE. *Terebenthina. Térébenthine. Terpentin.*—This term is applied to several oleoresins exuding from coniferous trees; also to the semifluid resin of *Pistacia Terebinthus*, a tree belonging to the terebenthaceous order. To obtain the turpentine, incisions are made in the bark of the trees, and the resinous juice, which exudes chiefly during the summer, is collected; it is then rendered more fluid by warming with water, and strained through straw-filters, to free it from needles, bark, and other extraneous substances.

The several varieties of commercial turpentine, obtained from fir- and pine-trees, are more or less viscid solutions of resins in a volatile oil, the proportions of these constituents varying according to the source and age of the turpentine. Some kinds are clear and homogeneous; others are more or less turbid, holding in suspension granulo-crystalline masses, which gradually settle to the bottom.

American turpentine, obtained chiefly from *Pinus australis*, and German turpentine from the Scotch fir (*Pinus sylvestris*), are yellowish, viscid, granular liquids, having a strong aromatic odour, and pungent bitter taste; they become clear when warmed, are highly inflammable, and burn with a very smoky flame. These turpentines consist of volatile oil and colophony (i. 1087); and on boiling them with water, the volatile oil goes off with the steam, while the resin remains, intimately mixed with small quantities of oil and water, forming a dingy yellow turbid mass, called "boiled turpentine," which is brittle when cold, but becomes soft and plastic when heated. At a stronger heat, the water and the remaining portion of volatile oil are given off, and the colophony remains as a transparent resin, more or less coloured, according to the degree of heat to which it has been exposed. Colophony was formerly said to be a mixture of two isomeric acid resins, pinic and sylvic acids (iv. 649, 650; v. 648); but the recent investigations of Maly (Ann. Ch. Pharm. cxxxii. 249; Jahresb. 1864, p. 408), have shown that it consists mainly of abietic anhydride, $C^{44}H^{62}O^4$, which, when treated with aqueous alcohol, takes up water, and is converted into abietic acid, $C^{44}H^{64}O^5$.*

French turpentine (from *Pinus maritima*) resembles American turpentine in appearance, odour, and taste. It hardens with calcined magnesia more readily than any other kind of turpentine.

Strasburg turpentine is a clear non-granular liquid, obtained from the silver fir (*Abies pectinata*), and from the spruce-fir (*Abies excelsa*). The turpentine from the former of these trees is mobile, yellow, has a pleasant odour of lemon, and a sharp bitter taste. That from the spruce-fir is dark-yellow, has a strong balsamic odour, and sweetish aromatic taste. The resinous portion of both these turpentines contains abietic acid, together with two indifferent resins, one (abietin) soluble in absolute alcohol, the other insoluble. The water with which these turpentines are distilled to get off the volatile oil, is said to contain succinic acid.

Venice turpentine—*Terebenthina venetia*, s. *laricina*, from the larch (*Larix europæa*)—is said to be contained in peculiar sacs in the upper part of the stem, and to be obtained by puncturing them. It is a ropy liquid, colourless, or brownish inclining to green, having a somewhat unpleasant odour, and bitter taste. According to

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* The formula given for abietic acid at p. 1 vol. i. belongs properly to sylvic acid, which is produced from abietic acid by the action of dilute sulphuric acid. The acid formerly designated as sylvic acid is regarded by Maly as impure hydrated abietic acid, and the so-called pinic acid as abietic anhydride.

Unverdorben (Pogg. Ann. xi. 27), it contains, in the fresh state, two oils of different degrees of volatility, the less volatile being easily resinised; also two acid resins, a neutral resin, and succinic acid.

Hungarian turpentine, which flows from incisions in the branches of *Pinus Pumilio*, is a clear, yellowish, mobile liquid, having an aromatic taste and odour.—Carpathian turpentine, from *Pinus Cembra*, resembles the last, but has a bitter taste.—Canadian turpentine, or Canada balsam, from *Abies balsamea*, has been already described under BALSAMS (i. 492).

Cyprian, Syrian, or Chio turpentine, obtained in Chio from *Pistacia terebinthus*, and in Syria from *P. vera*, is either clear and colourless, or, perhaps from age, or from want of care in collecting it, viscid, turbid, and yellowish-green; it has an odour of fennel and elemi, and an aromatic taste like that of mastic. It dissolves completely in ether, and partially in alcohol, leaving a glutinous residue.

Ordinary turpentine and Venice turpentine are used in medicine, both externally as ingredients of salves and plasters, and internally in the form of electuaries or pills; for the last-mentioned purpose, the turpentine is thickened by addition of magnesia; boiled turpentine (p. 920) is also made into pills. Many kinds of turpentine are also used for varnishes or similar purposes.

TURPENTINE, BOILED. See p. 919.

TURPENTINE CAMPHOR. A term applied sometimes to the solid monohydrochlorate, sometimes to the solid hydrates of turpentine-oil (p. 923).

TURPENTINE GALL-NUTS. *Gallæ pistacinæ. Carobe de Juda*; formerly designated as *Folliculi pistacinæ*. Pea-shaped or horny excrescences, occurring in August on the branches of the turpentine-chestnut (*Pistacia Terebinthus*), and formed by the puncture of an insect (*Cephis Pistaciæ*). They are reddish-brown, having an aromatic turpentine-like odour, and similar taste. They contain resin, volatile oil, tannin, and gallic acid. The ash contains a potassium-salt, silica, and lime. (Martius, Ann. Ch. Pharm. xxi. 179.—Guibourt, Pharm. Centr. 1844, p. 409.)

TURPENTINE, OIL OF. $C^{10}H^{16}$.—A volatile oil contained in the wood, bark, leaves, and other parts of pines, firs, and other trees belonging to the coniferous order, and separable therefrom by distillation with water. It is usually prepared by distilling crude turpentine (p. 919), either alone or with water. It was formerly supposed that all the volatile oils thus obtained, and having a composition represented by the formula $C^{10}H^{16}$, were identical in physical and chemical properties; but recent investigations, especially those of Berthelot,[*] have shown that the turpentine-oils obtained from different sources exhibit considerable diversities in their physical and more especially in their optical properties; further, that most kinds of turpentine-oil are mixtures of two or more isomeric or polymeric hydrocarbons, differing in physical and sometimes also in chemical properties. These modifications are often produced by the action of heat and of chemical reagents during the purification of the oil.

The following varieties of turpentine-oil are distinguished:—

1. French turpentine-oil, obtained from the French or Bordeaux turpentine of *Pinus maritima*.
2. English turpentine-oil, from the turpentine collected in Carolina, and other southern states of the American Union, from *Pinus australis* and *P. Tæda*.
3. German turpentine-oil, chiefly from the turpentine of *Pinus sylvestris*, *P. nigra*, and *P. rotundata*.
4. Venetian turpentine-oil, from Venice turpentine, the produce of *Larix europæa*.
5. Templin or Pine-cone oil, obtained from the cones of *Pinus Pumilio*, and, in some parts of Switzerland, from those of *Abies pectinata*.

Related to the true turpentine-oils are also two volatile oils, likewise obtained from coniferous plants—viz., oil of juniper from *Juniperus communis*, and oil of savine from *Juniperus Sabina*.

The several varieties of turpentine-oil, when purified by repeated rectification with water, are colourless mobile liquids, having a peculiar aromatic but disagreeable odour. They are insoluble in water, slightly soluble in aqueous alcohol, miscible in all proportions with absolute alcohol, ether, and carbonic disulphide. They dissolve iodine, sulphur, phosphorus, and many organic substances which are insoluble in water, such as fixed oils and resins, and are therefore used for making varnishes.

The diversities of character exhibited by turpentine-oils of different origin, relate chiefly to the specific gravity, boiling-point, and optical rotatory power. It must be remembered, however, that the substances designated as turpentine-oils are often mixtures of several substances, so that these properties may vary even in turpentine-oils of the same origin, according to the modes of preparation and purification adopted.

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[*] Ann. Ch. Pharm. lxxxiii. 105; lxxxviii. 345; cx. 367; Suppl. ii. 226; further, *Traité de Chimie organique*, ii. 692, 716—753. For references to earlier researches on turpentine-oil, see Gmelin's *Handbook*, xiv.

The specific gravity of turpentine-oils usually varies from 0·86 to 0·88. Their boiling-points are always near 160°. The rotatory power varies considerably: *e.g.*—

For English turpentine-oil . . $[\alpha] = +18{\cdot}6^{\circ}$
„ French „ . . $[\alpha] = -35{\cdot}4^{\circ}$
„ Venetian „ . . $[\alpha] = -5{\cdot}2^{\circ}$
„ Templin-oil . . . $[\alpha] = -76{\cdot}9^{\circ}$

The rotatory power of turpentine-oil is independent of that of the turpentine from which it is prepared. Thus, for example, English turpentine-oil is dextrorotatory, whereas the turpentine from which it is prepared is lævorotatory. Venice turpentine turns the plane of polarisation to the right, whereas the volatile oil distilled therefrom turns it to the left, &c.

The principal constituents of French and English turpentine-oils have been more particularly examined by Berthelot (*loc. cit.*).

French turpentine-oil consists mainly of a hydrocarbon, $C^{10}H^{16}$, called by Berthelot terebenthene. This substance cannot, however, be readily obtained from the commercial oil, in which it is contaminated with numerous products of transformation; but it may be prepared in a state of purity, by neutralising French turpentine with an alkaline carbonate, and distilling it, first over the water-bath, and then in a vacuum. By this treatment, all transformation of the product by heat, or by reagents, is avoided, and a hydrocarbon is obtained of constant physical character. Terebenthene thus prepared is a liquid of specific gravity 0·864, boiling at 161°, and having a specific rotatory power $= -42{\cdot}3^{\circ}$.

Australene, or Austraterebenthene, the chief constituent of English turpentine-oils, prepared in like manner from the turpentine of *Pinus australis*, is also a liquid, having the same specific gravity and boiling-point as terebenthene, but a specific rotatory power $= +21{\cdot}5^{\circ}$.

French turpentine-oil likewise contains an isomeric hydrocarbon, terepentilene, boiling below 180°, and another called parterebenthene, polymeric with terebenthene, which boils at about 250°. English turpentine-oil contains, besides australene, an isomeric body called austrilene. (Berthelot.)

Decompositions.—1. Turpentine-oil absorbs the *oxygen* of the air, becoming thicker, and ultimately resinous; at the same time, carbonic, acetic, and formic acids are produced. In this gradual oxidation, as in all slow combustions, part of the atmospheric oxygen is converted into ozone: hence turpentine-oil, after prolonged exposure to the air, always contains oxygen and ozone in solution, together with a continually increasing quantity of an oxygenated compound. When turpentine-oil containing water is exposed for some time to the sun's rays, in a large flask filled with oxygen, which is renewed from time to time, a hydrated oxide of turpentine-oil, $C^{10}H^{16}O.H^2O$, is deposited on the sides of the vessel, in stellate groups of long needles, soluble in hot water, also in alcohol and in ether. (Sobrero, Ann. Ch. Pharm. lxxx. 106.)

2. *Chlorine* is absorbed by turpentine-oil, with evolution of heat, sometimes sufficient to produce inflammation. When paper soaked in rectified turpentine-oil is introduced into a vessel filled with chlorine, the turpentine takes fire, and a quantity of black smoke is produced, together with white fumes of hydrochloric acid.—*Bromine* acts in a similar manner.—*Iodine* is dissolved by turpentine-oil, forming at first a green solution, which afterwards becomes hot, and gives off hydriodic acid. When a considerable quantity of iodine is suddenly brought in contact with turpentine-oil, explosion frequently ensues. Turpentine-oil distilled with *chloride of lime* and *water*, yields chloroform.

3. Turpentine-oil is rapidly attacked by *nitric acid*, the concentrated acid often setting it on fire. On evaporating the solution to dryness, and then distilling, the distillate contains nitrobenzene (Schiff, Ann. Ch. Pharm. cxiv. 201). If the nitric acid solution be precipitated with water, and the separated resin distilled with potash, toluidine passes over, together with other products (Chautard, *ibid.* lxxxviii. 340). In both these reactions, therefore, products are formed belonging to the class of aromatic compounds. When turpentine-oil is boiled for some time with moderately strong nitric acid, numerous products of decomposition are obtained, the formation of which has not yet been explained: nitrogen, carbonic oxide, carbonic dioxide, and hydrocyanic acid are evolved as gases; formic, acetic, propionic, and butyric acids distil over; and the residue contains oxalic acid, terebic acid (p. 723), camphretic acid,

(described under PYROCAMPHRETIC ACID, iv. 757), terephthalic acid, (p. 723), terebenzic acid (p. 723), and terechrysic acid (p. 725).

5. Turpentine-oil heated with *litharge* takes up a large quantity of oxygen, yielding formate and terebentate of lead. On washing the precipitate with alcohol, suspending it in water, decomposing it with sulphydric acid, exhausting the remaining solid substance with alcohol, and leaving the alcoholic solution to evaporate, white crystals are obtained, consisting of terebentic acid, $C^8H^{14}O^4$. (Weppen, Ann. Ch. Pharm. c. 253.)

6. The action of other acids, salts, &c., which combine directly with turpentine-oil, or merely convert it into isomeric or polymeric modifications, will be considered further on.

Compounds of Turpentine-oils with Hydrochloric, Hydrobromic, and Hydriodic Acids.

Hydrochlorates.—The terebenthenes, subjected to the action of hydrochloric acid gas, yield a mixture of crystallisable and liquid monohydrochlorates, $C^{10}H^{16}.HCl$. When they are left for some time in contact with fuming hydrochloric acid, or when their ethereal or alcoholic solution is saturated with hydrochloric acid, water then added, and the liquid left exposed to the air, a crystallisable dihydrochlorate, $C^{10}H^{16}.2HCl$, is produced; sometimes, also, unstable compounds of several hydrochlorates are obtained. The dihydrochlorates are likewise produced by the action of hydrochloric acid upon the hydrates of turpentine-oil, and by that of the chlorides of phosphorus on terpin-hydrate and terpin (p. 923).

The monohydrochlorates are optically active, producing rotation to the right or left, according to the nature of the terebenthene from which they have been formed: thus for the solid monohydrochlorate of terebenthene, $[\alpha] = -32{\cdot}2^\circ$; for that of australene, $[\alpha] = +11{\cdot}7$.—The dihydrochlorate is optically inactive.

The several varieties of turpentine-oil, inasmuch as they consist essentially of terebenthenes, likewise react with hydrochloric acid in the manner just described; indeed, most of the published statements respecting the hydrochlorates of turpentine-oil relate to products which have been prepared from turpentine-oils of unknown origin.

Solid Monohydrochlorate, $C^{10}H^{16}.HCl$.—This compound, also called artificial camphor, was discovered by Klein, in 1803. It is prepared by saturating rectified turpentine-oil with hydrochloric acid, keeping the liquid cool, pressing the crystals which separate after some hours, and recrystallising them from hot alcohol, or precipitating the alcoholic solution with water. It forms white crystals or crystalline flocks; by slow sublimation, it may be obtained in tufts of needles or shining laminæ. It resembles common camphor in appearance and in odour, and sublimes easily at ordinary temperatures. It melts at 115°, and boils, with partial decomposition, at 16·5°. It is insoluble in water, easily soluble in alcohol (especially at the boiling heat), and in oil of turpentine. At ordinary temperatures, it is very stable, not giving up its chlorine even to silver-salts; but when heated, it is decomposed by water and alcohol (at 160°), though not completely. The hydrochlorate is likewise decomposed when heated with salts, the decomposition sometimes requiring rather a high temperature. The product is always a hydrocarbon of the formula $C^{10}H^{16}$—viz. camphene, inactive camphene, or camphilene (pp. 924, 925).

Liquid Monohydrochlorate, $C^{10}H^{16}.HCl$ (sometimes called hydrochlorate of terebene).—Produced, together with the solid monohydrochlorate, by the action of hydrochloric acid gas on turpentine-oil, the proportion of the liquid hydrochlorate being greater as the temperature at which the reaction takes place is higher. To purify it, the liquid decanted from the solid hydrochlorate is cooled to −10°, in order to remove the portion of solid hydrochlorate still remaining in solution, then warmed for some time in the water-bath, treated with chalk, dissolved in twice its volume of alcohol, decolorised with animal charcoal, precipitated with water, and dried over chloride of calcium. It is a colourless, optically active oil, of specific gravity 1·017. It is decomposed by heating with salts, or with bases, but the hydrocarbon (camphilene, p. 925), which is the direct product of the decomposition, has not been further examined. By distillation over quicklime, it yields the so-called terpilene (p. 925).

Dihydrochlorate, $C^{10}H^{16}.2HCl$.—Produced when turpentine-oil is left for some time in contact with very strong hydrochloric acid (Berthelot); when terpin, terpin-hydrate, or terpinol is saturated with hydrochloric acid gas, or treated with the fuming acid (Deville, Ann. Ch. Pharm. lxxi. 351.—List, *ibid.* lxxvii. 369); also when terpin or terpin-hydrate is acted upon by a chloride of phosphorus (Oppenheim, *ibid.* cxxix. 149). When a solution of turpentine-oil in alcohol, ether, or acetic acid is saturated with hydrochloric acid, easily decomposible compounds of the dichlorhydrate with the solid or liquid monohydrochlorate are produced; and on adding water, and leaving the liquid for some time in contact with the air, crystals of the dihydrochlorate are obtained.

The dihydrochlorate forms rhombic tables, insoluble in water, easily soluble in boiling alcohol. It is slowly decomposed by boiling with water or alcohol, quickly by boiling with alcoholic potash-solution, yielding terpinol.

Hydrobromates.—Hydrobromic acid acts on turpentine-oil in the same manner as hydrochloric acid, forming a crystallisable and a liquid monohydrobromate, $C^{10}H^{16}.HBr$. A crystallisable dihydrobromate, $C^{10}H^{16}.2HBr$, melting at 42°, is produced by the action of phosphoric pentabromide on turpentine-oil. When hydrobromic acid gas is passed into a solution of turpentine-oil in acetic acid, a liquid compound of the two hydrobromates, $C^{10}H^{16}.HBr + C^{10}H^{16}.2HBr$, is formed; when exposed to the air, it yields crystals of the dihydrobromate. (Oppenheim, Ann. Ch. Pharm. cxxix. 149.)

Hydriodates.—Gaseous hydriodic acid does not appear to form a solid compound with turpentine-oil. The product, which is liquid and easily decomposible, appears to be a mixture of two hydriodates, one corresponding with the solid, the other with the liquid monohydrochlorate.

Terpin, treated with iodide of phosphorus (PI^3 or PI^2), yields the easily decomposible dihydriodate, $C^{10}H^{16}.2HI$, which crystallises from ethereal solution, in colourless hexagonal tables melting at 48°. (Oppenheim.)

Hydrates of Turpentine-oil.

The terebenthenes unite with water in several proportions, yielding the following compounds:

$C^{10}H^{16}.3H^2O$	$C^{10}H^{16}.2H^2O$	$C^{10}H^{16}.H^2O$	$2C^{10}H^{16}.H^2O.$
Terpin-hydrate.	Terpin.	Terpentin-hydrate.	Terpinol.

Terpin-hydrate, $C^{10}H^{16}.2H^2O$. aq. (also called *Turpentine-camphor* and *Hydrate of Turpentine-oil*), is frequently deposited in crystals from turpentine-oil containing water; its production is favoured by the presence of an acid. To prepare it, 8 vols. turpentine-oil are mixed with 2 vols. nitric acid and 1 to 6 vols. alcohol; and the mixture is frequently shaken during the first few days, then left to itself in shallow vessels for several weeks. Brown crystals are thereby formed, which must be pressed, and then recrystallised from boiling water, with addition of animal charcoal.

Terpin-hydrate usually crystallises in large rhombic prisms; it dissolves sparingly in cold, easily in boiling water, easily also in alcohol and ether. At 100° it melts, gives off its water of crystallisation, and is converted into terpin. The same change takes place on exposing the crystals to air dried over oil of vitriol.

Terpin, $C^{10}H^{16}.2H^2O$, melts at 103°, and solidifies in the crystalline state on cooling. It sublimes at about 150°, in slender needles. It is dissolved with red colour by *strong sulphuric acid*, and converted into turpentine-oil. The same change takes place on boiling the terpin with *dilute acids*, heating it to 100° with *chloride of zinc*, or to 160°—180° with *chloride of calcium, strontium*, or *ammonium*. Terpin, or terpin-hydrate, subjected to the action of gaseous or aqueous *hydrochloric acid*, or of either of the *chlorides of phosphorus*, is converted into the crystallised dihydrochlorate, $C^{10}H^{16}.2HCl$. Terpin, distilled with *phosphoric anhydride*, yields terebene and colophene (p. 924). When vapour of terpin is passed over *soda-lime*, heated to 400°, terebentilic acid (p. 723) is produced. Heated with *acetic* or *butyric acid*, or with *benzoic chloride*, it yields terebene and polyterebenes (p. 924). When heated with *acetic anhydride* to 140°, for not too long a time, it yields a compound containing $C^{10}H^{16}.C^2H^4O^2.H^2O$, regarded by Oppenheim as an acetic ether, $\left.\begin{matrix}(C^{10}H^{18})''\\ C^2H^3O\\ H\end{matrix}\right\}O^2$. This compound boils at 140°—150°, under a pressure of 2 centimetres of mercury.

Terpinol, $2C^{10}H^{16}.H^2O$. (Wiggers, Ann. Ch. Pharm. lvii. 247.—List, *ibid.* lxvii. 367.—Oppenheim, cxxix. 155.)—Produced when terpin is boiled or distilled with dilute hydrochloric or sulphuric acid; also when the dihydrochlorate of terebenthene is boiled with water, alcohol, or alcoholic potash. It is a colourless, strongly refracting oil, having a pleasant odour of hyacinths, slightly soluble in water, and optically inactive. Specific gravity = 0·852. It boils at about 168°, but suffers partial decomposition at the same time, and in such a manner, that the first portions of the distillate contain less oxygen than the later portions. It forms with hydrochloric acid the crystallisable dihydrochlorate, $C^{10}H^{16}.2HCl$, and may be reconverted into terpin by assumption of water.

Terpentin-hydrate, $C^{10}H^{16}.H^2O$. *Liquid Turpentine-camphor.*—This compound is sometimes obtained in the preparation of terpin, either together with the latter, or forming the only product. It is a liquid insoluble in water; boils, apparently without decomposition, at 200°—220°, and in presence of water appears to be converted, under circumstances not exactly understood, into terpin. It is optically active; $[\alpha] = -42{\cdot}4°$. When treated with hydrochloric acid, it yields the crystallisable dihydrochlorate, $C^{10}H^{16}.2HCl$. (Deville, Ann. Ch. Pharm. lxxi. 348.)

Molecular Transformations of Turpentine-oil.

I. By heat.—Terebenthene (p. 922) when carefully prepared, may be distilled, and even heated considerably above its boiling-point, without alteration; but towards 250°, it begins to undergo a change, the boiling-point rising, the rotatory power diminishing, and the product becoming more easily oxidisable in contact with the air; this alteration goes on the more rapidly as the temperature is higher. The product consists of one isomeric and several polymeric modifications of terebenthene.

The isomeric modification, called terepyrolene, resembles austrapyrolene, but has not been particularly examined. The chief product is the polymeric modification metaterebenthene, $C^{20}H^{32}$. It is a yellowish viscid liquid, boiling at about 360°, and of specific gravity 0·913. It forms, with hydrochloric acid, the liquid compound $C^{20}H^{32}.HCl$.

Australene (p. 921), heated for several hours to 250°, is converted into the isomeric body, austrapyrolene, boiling at 177°, and having a specific gravity of 0·847, and specific rotatory power = −11°. It smells like lemon-oil, is more readily oxidisable than australene, and forms a solid hydrochlorate, $2C^{10}H^{16}.3HCl$, which has a specific rotatory power of −14·6°. By continued heating, the polymeric body, metaustraterebenthene, is produced, very much like metaterebenthene, having a specific gravity of 0·91, and boiling at about 360°; its specific rotatory power is smaller than that of australene, and of opposite sign.

II. By reagents.—Many substances possess the power of converting terebenthene into isomeric or polymeric modifications. Some act even at ordinary temperatures, others only with the aid of heat. Many produce the transformation in a very short time; others act slowly, and never produce complete transformation. In some cases very small quantities of the reagent are sufficient to produce complete transformation, but frequently large quantities are required. The most energetic reagent is *fluoride of boron*. 1 pt. of this substance instantly converts 160 pts. terebenthene, with great rise of temperature, into polymeric optically inactive modifications, boiling above 300°.—*Sulphuric acid* likewise acts in the cold, but less energetically; 1 pt. of this acid converts 4 pts. terebenthene into an isomeric and a polymeric modification.—Weak mineral acids (like *boric acid*), and several organic acids (e.g., *acetic, oxalic, tartaric,* and *citric acids*), act upon terebenthene at 100°; but the action is very slow, and not complete, even after 50 or 60 hours.—*Chloride of zinc*, at 100°, acts in a similar manner.—*Fluoride* and *chloride of calcium*, and even the *chlorides of the alkali-metals*, act in like manner, but very feebly; the transformation takes place, however, more quickly in presence of these substances than under the influence of heat alone.

The products of these transformations are the same in all cases, viz.:

α. Terebene, an isomeric modification.—This substance is best prepared by the action of strong sulphuric acid on terebenthene or australene, and may therefore also be obtained from turpentine-oil. The process consists in mixing the turpentine-oil with $\frac{1}{20}$th of its weight of strong sulphuric acid, leaving the liquid to stand for twenty-four hours, then decanting it from the sediment, and distilling; repeating the process till the product no longer acts on polarised light; then washing with water and carbonate of sodium, drying over chloride of calcium, and rectifying.

Terebene is a liquid having the odour of thyme-oil, a specific gravity of 0·864, boiling at 156°, optically inactive. With hydrochloric acid, it forms a liquid compound, $2C^{10}H^{16}.HCl$, and similar compounds with hydrobromic and hydriodic acids.

β. A liquid optically inactive hydrocarbon, boiling at 250°, and probably consisting of sesquiterebene, $C^{15}H^{24}$.

γ. Diterebene, Metaterebene, or Colophene, $C^{20}H^{32}$.—Produced, together with terebene, in the process above described. It is an oil, having an aromatic odour, a blue iridescence, optically inactive, of specific gravity 0·94, boiling at 310°—315°. It absorbs hydrochloric acid gas, but does not appear to form a definite compound with it. Chlorine converts it into a resinous mass, from which alcohol extracts a compound crystallising in yellow needles, and probably consisting of a substitution-product, $C^{20}H^{28}Cl^4$. (See i. 1086.)

δ. Various polyterebenes, $(C^{10}H^{16})^n$.—Optically inactive liquids, of continually increasing viscidity, and boiling at temperatures between 360° and a low red heat.

III. By combination with hydrochloric acid or water, and decomposition of these compounds.

The solid monohydrochlorates of turpentine-oil, subjected to the action of very weak reagents, yield hydrocarbons, $C^{10}H^{16}$, designated by Berthelot as **camphenes**.[*] The three following are known:—

1. **Terecamphene.**—Produced by heating the solid hydrochlorate, prepared from French turpentine-oil, to 200°—220°, for a considerable time, with stearate of potassium or dry soap. The product, purified by recrystallisation from alcohol, is solid and crystallisable, with the aspect of camphor. It melts at 45°, and boils at about 160°. Specific rotatory power $[\alpha] = -65°$. It forms only one compound with hydrochloric acid, namely, a solid monohydrochlorate, $C^{10}H^{16}.HCl$, whose specific rotatory power is $+32$; that is to say, equal and opposite to that of the solid monohydrochlorate of terebenthene.

2. **Austracamphene.**—Obtained from English turpentine-oil in the same way as terecamphene is obtained from the French oil. It resembles terecamphene in all its properties, excepting in its optical rotatory power, which is $[\alpha] = +22°$. It forms a solid monohydrochlorate, having a specific rotatory power of $-5°$.

3. **Inactive Camphene.**—This is a solid hydrocarbon, produced by treating turpentine-oil, in the manner above described, with stearate of barium, or better with benzoate of sodium: it resembles terecamphene in every particular, excepting in its relation to polarised light. It forms a solid monohydrochlorate, which is likewise inactive.

Camphilene.—This name is given by Berthelot to a hydrocarbon (not yet examined), which is produced by the action of potassium-stearate or other weak reagents on the liquid monohydrate of terebenthene.

The same name (also *Dadyl*) is applied to a hydrocarbon (evidently a product of the transformation of camphene), formed by distilling the solid monohydrochlorate of turpentine-oil several times over quicklime, or in the state of vapour over lime heated to 190°—195°. It is a limpid aromatic liquid, of specific gravity 0·87, boiling at 156°, and without action on polarised light. According to Laurent, it forms, with chlorine, the compound $C^{10}H^{15}Cl.HCl$, which, when treated with alcoholic potash, yields chlorocamphilene, $C^{10}H^{15}Cl$; and this again unites with chlorine, forming the compound $C^{10}H^{14}Cl^2.HCl$, &c.: hence it would appear that camphilene reacts with chlorine in the same manner as ethylene.

Terpilene.—An inactive hydrocarbon, produced by the action of weak reagents on the solid dihydrochlorate, $C^{10}H^{16}.2HCl$.

Terebilene is a hydrocarbon obtained by distilling the liquid monohydrochlorate of turpentine-oil with quicklime or with potassium; also by distilling the corresponding hydriodate with potash. It smells like terebene, and is optically inactive. Specific gravity = 0·843. Boiling-point = 134°.

Substitution-products of Turpentine-oils.

Chlorine forms, with turpentine-oil, a liquid having a camphorous odour, and turning the plane of polarisation to the right, even when it has been prepared from lævo-rotatory turpentine-oil. It appears to be a mixture of tetrachlorinated turpentine-oil and tetrachloroterebene.

When chlorine is passed over the solid monohydrochlorate of turpentine-oil, a yellow liquid is formed, consisting of $C^{10}H^{12}Cl^4.HCl$, and easily resolved into hydrochloric acid and tetrachlorinated turpentine-oil, $C^{10}H^{12}Cl^4$. The latter is crystalline, melts at 110°—115°, and decomposes at a higher temperature. It is optically inactive.

Terebene also forms substitution-products with chlorine, chiefly tetrachloroterebene.

Bromine acts on turpentine-oil and terebene similarly to chlorine, forming chiefly tetrabrominated products.

The products of the action of chlorine on camphilene have already been mentioned.

TURPENTINE-VARNISHES. Solutions of resins in oil of turpentine.

TURPETH or **TURBITH MINERAL.** An old name for basic mercuric sulphate, $HgSO^4.2HgO$ (p. 605). Sulphate of tetramercurammonium, $(N^2Hg^4)SO^4.2H^2O$, is sometimes called *ammoniacal turpethum*.

TURPETH or **TURBITH ROOT.** The root of *Convolvulus Turpethum*, or *Ipomæa Turpethum*, a plant indigenous in India and Australia. It has a disagreeable sweetish taste, and contains, according to Boutron-Charlard (J. Pharm. viii. 131), a volatile oil, fat, a yellow colouring-matter and a drastic resin. This resin constitutes about 4 per cent. of the root, and contains about $\frac{1}{20}$th of its weight of a substance soluble in ether, the remaining $\frac{19}{20}$ths consisting of **turpethin**. (Spirgatis.)

[*] The term "camphene" is commonly used as a generic name for the hydrocarbons, $(C^{10}H^{16})$, (see i. 724). If it be restricted to the meaning above given, the entire group may be designated as **terpenes**.

TURPETHIC ACID. $C^{34}H^{60}O^{18}$. (Spirgatis, J. pr. Chem. xcii. 97: Jahresb. 1864, p. 591.)—An acid produced by the action of bases on turpethin, $C^{34}H^{56}O^{16}$. When turpethin is dissolved in warm baryta-water, the baryta removed by sulphuric acid, the excess of this acid by lead-hydrate, the latter by sulphydric acid, and the filtrate evaporated, turpethic acid remains as an amorphous yellowish mass, easily soluble in water, having a strong acid reaction, and a bitter somewhat sour taste. It forms two barium-salts, containing $C^{34}H^{58}Ba''O^{18}$ and $C^{34}H^{58}Ba''O^{18}.C^{34}H^{60}O^{18}$. It is resolved by mineral acids into glucose and turpetholic acid.

TURPETHIN. $C^{34}H^{56}O^{16}$. (Spirgatis, *loc. cit.*)—A purgative resin, isomeric with jalapin and scammonin, extracted from the root of *Ipomœa Turpethum* (*vid. sup.*). To prepare it, the root is exhausted with cold water: the dried residue is treated with alcohol, the alcoholic extract concentrated by distillation; the residue mixed with water; and the brown-yellow mass thereby precipitated is repeatedly boiled with water, then dried and shaken up four or five times with ether, and repeatedly precipitated by ether from solution in absolute alcohol.

Turpethin thus prepared is a brownish-yellow inodorous resin, gradually exciting a sharp bitterish taste, and strongly irritating the mucous membranes of the mouth and nose when pulverised. It dissolves easily in alcohol, like jalapin, but is distinguished from that substance by its insolubility in ether. It melts at about 183°, and dissolves slowly in strong sulphuric acid, forming a red liquid. When treated with alkalis, baryta-water for example, it takes up 2 at. water, and is converted into turpethic acid. Under the influence of mineral acids, it is redissolved into glucose and turpetholic acid:

$$C^{34}H^{56}O^{16} + 6H^2O = 3C^6H^{12}O^6 + C^{16}H^{32}O^4.$$

TURPETHOLIC ACID, $C^{16}H^{32}O^4$, separates, in the reaction just described, as a yellowish-white granular conglomerate; and after washing with water, and repeated crystallisation from dilute alcohol, with addition of animal charcoal, forms a white mass, made up of slender microscopic needles. It is inodorous, has an irritating taste and acid reaction, dissolves easily in alcohol, less easily in ether, melts at about 88°, and decomposes at a stronger heat, like jalapinolic acid (iii. 440) giving off a white fume which strongly irritates the eyes and nose.—*Turpetholate of Sodium*, $C^{16}H^{31}NaO^4$, is a white mass, having a silky lustre, and exhibiting, under the microscope, sharply defined rhombic plates, with angles of about 55° and 125°.—The *barium-salt*, $C^{32}H^{62}Ba''O^8$, is amorphous. (Spirgatis.)

TURRITE. Syn. with RUTILE.

TUSSILAGO. The root of *Tussilago Petasites*, L. (*Petasites vulgaris*, Desf.) contains, according to Reinsch (N. Jahrb. Pharm. iv. 257), a volatile oil, a crystallisable acid resin, called resinapitic acid, another resin called petasite, the alcoholic solution of which forms, with mineral acids, an emerald-green liquid, afterwards turning blue when hydrochloric acid is used,—besides glucose, mannite, inulin, tannin, and the ordinary plant-constituents.

TURQUOIS. A native hydrated aluminium-phosphate, $2Al^2O^3.P^2O^5.5H^2O$, found in Persia, and much valued as a gem. (See PHOSPHATES, iv. 552.)

TYPE-METAL. Printers' types are made of an alloy of lead and antimony, sometimes with addition of zinc or bismuth, and of tin for stereotype plates (i. 316; iii. 532).

TYPES, CHEMICAL. Bodies analogous in constitution, and exhibiting analogous reactions, are said to belong to the same type. Thus hydrochloric acid, HCl, or rather its multiple nHCl, may be taken as the type of chlorides, which may, in fact, be derived from it by equivalent substitution: *e.g.* KCl, $Ba''Cl^2$, $Sb'''Cl^3$, $Si^{iv}Cl^4$, $As^{v}Cl^5$, &c. In like manner, the sulphates are derived from the type nH^2SO^4, the orthophosphates from the type nH^3PO^4, metaphosphates from $nHPO^3$, &c. In a wider sense, the formula HCl may be taken as the type of chlorides, bromides, iodides, fluorides, and cyanides; H^2O of oxides, sulphides, selenides, tellurides, oxysalts, sulphur-salts, &c.; and H^3N of all amines and amides, and of the corresponding phosphorus, arsenic, and antimony compounds. It is unnecessary to go further into detail on this subject, as it has been fully explained in the article CLASSIFICATION (i. 1007), and, moreover, the system of formulation according to types has been adopted throughout this work. In the present article we shall endeavour to give a sketch of the history of the theories of types and substitution.

GAY-LUSSAC observed that wax, when bleached by chlorine, [illegible] gives up hydrogen, [illegible] of chlorine equal to that of the hydrogen [illegible] removed. Dumas [illegible] with oil of turpentine; and by ext[illegible] ending the investigation to the action of chlorine, bromine, and other elements on various organic substances, he concluded that:—*When a body containing hydrogen is subjected to the dehydrogenising influence of chlorine, bromine, iodine, oxygen, &c., it takes up, for every atom of hydrogen removed, an atom of chlorine, bromine, iodine, or oxygen* [O = 8].

The announcement of this empirical law of substitution gave rise to a large number of experiments in the same direction, especially by Laurent, who first instituted a careful comparison between the properties of the substitution-product and those of the primitive compound, and thence concluded that:—*When equivalent substitution of hydrogen by chlorine or bromine takes place, the chlorine or bromine takes up the position previously occupied by the hydrogen, and plays to a certain extent the same part, so that the chlorinated or brominated product is analogous in constitution to the body from which it has been formed.*

Dumas was at first opposed to this idea, as to the part which the chlorine plays in these substitutions; but afterwards, when a larger number of substitution-products had been obtained (by Laurent, Malaguti, Regnault, and others), and when he himself had discovered trichloracetic acid, and shown it to be analogous in all its reactions to acetic acid, he not only adopted Laurent's views, but even went beyond them, extending them to substitutions by oxygen, and developing them into the theory of types, the main principles of which he laid down, in 1839, as follows:—

1. The elements of a compound may, in numerous cases, be replaced, in equivalent proportions, by other elements, and by compound bodies which play the part of elements.

2. When this substitution takes place in equal numbers of equivalents, the body in which the substitution retains its chemical type, and the elements which have entered into it, play therein the same part as the element which has been abstracted.

The chemical type included bodies containing the same number of atoms of their elements, and resembling one another in their principal chemical properties—such as acetic and trichloracetic acids, or chloroform, bromoform, and iodoform. When, on the other hand, the chemical character of a body was altered by substitution, the number of elementary atoms remaining the same, the two bodies were regarded as belonging to the same mechanical or molecular type: *e.g.* marsh-gas, CH^4; formic acid, CH^2O^2; chloroform, $CHCl^3$; chloride of carbon, CCl^4.

The law of substitution is the expression of facts, which the type-theory was intended to explain. It was not supposed that the type was preserved because substitution took place in equivalent proportions; but the permanence of the type was regarded as a power striving to retain the atoms in the original order, and thus giving to the substitution of one element another. According to this theory, the properties of a compound depend, in many cases, upon the relative positions of its atoms, much more than upon their individual nature.

These views were met with determined opposition by Berzelius and the other upholders of the electrochemical theory. According to that theory, chemical combination consists in the union of atoms or molecules in opposite electrical states, and the function of any element in a compound depends altogether on its electrical polarity. Such a theory is plainly irreconcilable with the idea that a strongly electronegative body like chlorine can take the place of a positive element like hydrogen, and discharge similar functions in the resulting compound. Accordingly, the advocates of the electrochemical theory at first denied the facts upon which the substitution-theory was founded; and afterwards, when these facts had been incontestably established by numerous analyses, sought to explain them in a manner consistent with the principles of the electrochemical theory. With this view, Berzelius endeavoured to show that acetic and trichloracetic acids are differently constituted compounds, acetic acid being an oxide of the radicle C^4H^3, whereas trichloracetic consists of oxalic acid "copulated" with chloride of carbon; thus:

Acetic acid	$C^4H^3.O^3 + HO$
Trichloracetic acid	$C^2Cl^3 + C^2O^3 + HO.$

The numerous substitution-products of acetic ether, formic ether, &c., discovered by Malaguti and Regnault, were likewise formulated by Berzelius in a similar manner: *e.g.*—

Dichlorethylic ether .	$C^4H^3.O^3 + 2C^4H^3.Cl^3$
Perchlorethylic ether .	$C^2O^3 + 5C^2Cl^3$
Dichloracetic ether . .	$2C^4H^3.O^3 + C^4H^3.Cl^3$
Dichloroformic ether .	$2C^2H.O^3 + C^2H.Cl^3 + 2C^4H^3.O^3 + C^4H^3.Cl^3$
Monochloromethyl-oxide .	$C^2H^3.O^3 + C^2H^3.Cl^3$
Dichloromethylic oxide .	$C^2H.O^3 + 2C^2H.Cl^3$
Perchloromethylic oxide .	$CO^2 + 3CCl^2$

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The chemical type included bodies containing the same number of atoms of their elements, and resembling one another in their principal chemical properties—such as acetic and trichloracetic acids, or chloroform, bromoform, and iodoform. When, on the other hand, the chemical character of a body was altered by substitution, the number of elementary atoms remaining the same, the two bodies were regarded as belonging to the same mechanical or molecular type: *e.g.* marsh-gas, CH^4; formic acid, CH^2O^2; chloroform, $CHCl^3$; chloride of carbon, CCl^4.

The law of substitution is the expression of facts, which the type-theory was intended to explain. It was not supposed that the type was preserved because substitution took place in equivalent proportions; but the permanence of the type was regarded as a power striving to retain the atoms in the original order, and thus giving to the substitution of one element another. According to this theory, the properties of a compound depend, in many cases, upon the relative positions of its atoms, much more than upon their individual nature.

These views were met with determined opposition by Berzelius and the other upholders of the electrochemical theory. According to that theory, chemical combination consists in the union of atoms or molecules in opposite electrical states, and the function of any element in a compound depends altogether on its electrical polarity. Such a theory is plainly irreconcilable with the idea that a strongly electronegative body like chlorine can take the place of a positive element like hydrogen, and discharge similar functions in the resulting compound. Accordingly, the advocates of the electrochemical theory at first denied the facts upon which the substitution-theory was founded; and afterwards, when these facts had been incontestably established by numerous analyses, sought to explain them in a manner consistent with the principles of the electrochemical theory. With this view, Berzelius endeavoured to show that acetic and trichloracetic acids are differently constituted compounds, acetic acid being an oxide of the radicle C^4H^3, whereas trichloracetic consists of oxalic acid "copulated" with chloride of carbon; thus:

Acetic acid	$C^4H^3.O^3 + HO$
Trichloracetic acid	$C^2Cl^3 + C^2O^3 + HO.$

The numerous substitution-products of acetic ether, formic ether, &c., discovered by Malaguti and Regnault, were likewise formulated by Berzelius in a similar manner: *e.g.*—

Dichlorethylic ether .	$C^4H^3.O^3 + 2C^4H^3.Cl^3$
Perchlorethylic ether .	$C^2O^3 + 5C^2Cl^3$
Dichloracetic ether . .	$2C^4H^3.O^3 + C^4H^3.Cl^3$
Dichloroformic ether .	$2C^2H.O^3 + C^2H.Cl^3 + 2C^4H^3.O^3 + C^4H^3.Cl^3$
Monochloromethyl-oxide .	$C^2H^2.O^2 + C^2H^2.Cl^2$
Dichloromethylic oxide .	$C^2H.O^3 + 2C^2H.Cl^3$
Perchloromethylic oxide .	$CO^2 + 3CCl^2$

But these complicated formulæ, which represented compounds evidently analogous in properties, as constituted in entirely different ways, met with little acceptance, more especially as, in order to carry out such modes of representation, it was necessary to invent a new radicle for almost every organic compound that was discovered; and finally, when **Melsens** showed that acetic acid can be reproduced from trichloracetic acid by the action of sodium-amalgam, the idea that these two bodies were differently constituted became altogether untenable. Accordingly, it was then assumed that, as trichloracetic acid was oxalic acid copulated with C^2Cl^3, so acetic acid itself was oxalic acid copulated with C^2H^3:

Acetic acid	. .	$C^2H^3 + C^2O^6 + HO$
Trichloracetic acid	.	$C^2Cl^3 + C^2O^6 + HO$;

and this view was supposed to be supported by the fact that chlorine took the place of hydrogen in the "copula." Similar formulæ were given for methyldithionic acid and the allied compounds discovered by Kolbe:

Trichloromethyldithionic acid	.	$C^2Cl^3 + S^2O^5 + HO$
Dichloromethyldithionic acid	.	$C^2HCl^2 + S^2O^5 + HO$;

and by this fanciful hypothesis of copulæ, the fact of substitution was supposed to be reconciled with the old theory. It is clear, however, that by this mode of explanation, the possibility of chlorine taking the place of hydrogen in a compound, and discharging similar functions therein, was substantially admitted; and thus the main point of the substitution-theory was established.

In this contest between the old radicle-theory and the substitution-theory, the adherents of the latter had somewhat overlooked the good points of the former, resorting almost exclusively to empirical formulæ to represent the relations of compounds. As, however, it was found that mere empirical formulæ did not always represent these relations so clearly as the hypothetical formulæ of the radicle-theory, endeavours were made to construct formulæ which should attain this end without requiring the use of the numerous hypotheses of the radicle-theory. This object was greatly promoted by certain considerations which **Gerhardt** put forward in 1839, and afterwards further developed under the name of "Theory of Residues." He says: "When a so-called replacement of an element by a compound body takes place, the process *is* not a direct substitution; but an element of the one body (*e.g.* H) unites with an element of the other (O), the resulting product (HO) separating out, while the remaining elements (residues) of the two bodies enter into combination." These residues are evidently identical, in many cases, with the radicles of the older theory, and exhibit the relations of compounds to one another with the same clearness, without the necessity of assuming the pre-existence of these radicles in the compounds. In short, the use of them in equations of decomposition shows that a group of elements, or in other words a radicle, may be substituted for an element in a compound, without altering the type.

This process of amalgamation of the radicle and type theories received a great stimulus, in the years 1849 and 1850, by the discovery of the alcoholic ammonia-bases by **Wurtz** and **Hofmann**, which showed that the hydrogen in ammonia, NH^3, may be replaced, partly or even wholly, by an equivalent quantity of the radicles ethyl, methyl, &c., forming bodies of the same nature as ammonia itself. These discoveries, which demonstrated, more clearly than any that had gone before, that organic bodies may be referred to simple inorganic compounds as types, may indeed be regarded as the foundation-stone of the modern type-theory.

Another very important step in the same direction was **Williamson's** discovery of the mixed ethers (1850), and his explanation of the general relations of the ethers and alcohols, by referring them to the type of water, H^2O (Chem. Soc. Qu. J. iv. 106, 229). **Williamson** subsequently extended these views to acids, representing acetic acid, for example, as $\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}O$; he also pointed out the possibility of replacing the second atom of hydrogen in the water-molecule by an acid radicle, thereby forming a compound related to acetic acid in the same manner as ether to alcohol (Chem. Soc. Qu. J. iv. 350).—This prediction was verified, in 1852, by Gerhardt's discovery of the anhydrides of acetic acid, benzoic acid, &c. From that time chemists vied with one another, in referring organic bodies to the simplest types of inorganic chemistry; and thus arose the views which were systematised by **Gerhardt** in the fourth volume of his *Traité de Chimie organique*, iv. 560—806. (See also Graham's *Elements of* [illegible]*istry*, 2nd edition, ii. 519—569, and the article CLASSIFICATION in this [illegible] 1015.)

It is usual at the present day to admit four principal types:

HH $\quad OH^2$ $\quad NH^3$ $\quad CH^4$;

or, more generally (denoting monatomic and polyatomic radicles by Roman numerals)

$I + I$ $\quad II + 2I$ $\quad III + 3I$ $\quad IV + 4I$;

and to these, together with the multiple and mixed types, formed by combining two or more of them together, nearly all well-defined compounds may be referred. Sometimes, however it is convenient to refer compounds to types containing radicles of higher atomicity; for example:

Type.	Phosphoric penta-chloride.	Phosphoric oxychloride.	Phosphoric acid.	Stibmethyl-oxide.	Tetrethyl-ammonium-chloride.
$V + 5I$	$P^{v}Cl^5$	$P^{v}\left\{\begin{matrix}Cl^3\\O''\end{matrix}\right.$	$P^{v}\left\{\begin{matrix}(HO)^3\\O''\end{matrix}\right.$	$Sb^{v}\left\{\begin{matrix}(C^2H^5)^3\\O''\end{matrix}\right.$	$N^{v}\left\{\begin{matrix}(C^2H^5)^4\\Cl\end{matrix}\right.$

Type.	Tungstic chloride.	Tungstic oxide.	Sulphuric oxide.	Sulphuric acid.	Sulphuric dibromo-ethylenic diethide.
$VI + 6I$	$W^{vi}Cl^6$	$W^{vi}O^3$	$S^{vi}O^3$	$S^{vi}\left\{\begin{matrix}(HO)^2\\O^2\end{matrix}\right.$	$S^{vi}\left\{\begin{matrix}(C^2H^4)''\\(C^2H^5)^2\\Br^2\end{matrix}\right.$

The union of two or more molecules of the same or different types, by the substitution of a polyatomic element or radicle for an equivalent number of hydrogen-atoms, gives a considerable extension to the power of typical representation; for example:

Type.	Phosphorous chloride.	Phosphoric oxychloride.	Trichlorhydrin.	Citric chloride.
$3HH$	PCl^3	$(PO)'''Cl^3$	$(C^3H^5)'''Cl^3$	$(C^6H^5O^4)'''Cl^3$

Type.	Sulphuric acid.	Succinic acid.	Oxalic acid.	Glycol.
$2H^2O$	$\left.\begin{matrix}(SO^2)''\\H^2\end{matrix}\right\}O^2$	$\left.\begin{matrix}(C^4H^4O^2)''\\H^2\end{matrix}\right\}O^2$	$\left.\begin{matrix}(C^2O^2)''\\H^2\end{matrix}\right\}O^2$	$\left.\begin{matrix}(C^2H^4)''\\H^2\end{matrix}\right\}O^2$

Type.	Phosphoric acid.	Citric acid.	Glycerin.
$3H^2O$	$\left.\begin{matrix}(PO)'''\\H^3\end{matrix}\right\}O^3$	$\left.\begin{matrix}(C^6H^5O^4)'''\\H^3\end{matrix}\right\}O^3$	$\left.\begin{matrix}(C^3H^5)'''\\H^3\end{matrix}\right\}O^3$

Type.	Oxamide.	Succinamide.	Ethylene-diamine.
$2H^3N$	$\left.\begin{matrix}(C^2O^2)''\\H^2\end{matrix}\right\}N^2$	$\left.\begin{matrix}(C^4H^4O^2)''\\H^2\end{matrix}\right\}N^2$	$\left.\begin{matrix}(C^2H^4)''\\H^2\end{matrix}\right\}N^2$

Type.	Sulphurous acid.	Sulpho-phenylic acid.	Methylsulphurous acid.
$\begin{matrix}H\\ \left\{\begin{matrix}H\\ \left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix}\right.\end{matrix}$	$\begin{matrix}H\\ \left.\begin{matrix}(SO^2)''\\H\end{matrix}\right\}O\end{matrix}$	$\begin{matrix}C^6H^5\\ \left.\begin{matrix}(SO^2)''\\H\end{matrix}\right\}O\end{matrix}$	$\begin{matrix}CH^3\\ \left.\begin{matrix}(SO^2)''\\H\end{matrix}\right\}O\end{matrix}$

Type.	Hyposulphurous acid.	Type.	Sulphuric chlorhydrate.
$\left\{\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O\\ \left.\begin{matrix}H\\H\end{matrix}\right\}S\end{matrix}\right.$	$\begin{matrix}\left.\begin{matrix}H\\(SO)''\end{matrix}\right\}O\\ \left.\begin{matrix}\\H\end{matrix}\right\}S\end{matrix}$	$\begin{matrix}HCl\\ \left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix}$	$\left.\begin{matrix}(SO^2)''\\H\end{matrix}\right\}\begin{matrix}Cl\\O\end{matrix}$

Type.	Sulphamic acid.	Carbamic acid.	Oxamic acid.
$\left.\begin{matrix}H^3N\\H^2O\end{matrix}\right\}$	$\begin{matrix}\left.\begin{matrix}H^2\\(SO^2)''\end{matrix}\right\}N\\ \left.\begin{matrix}H\end{matrix}\right\}O\end{matrix}$	$\begin{matrix}\left.\begin{matrix}H^2\\(CO)''\end{matrix}\right\}N\\ \left.\begin{matrix}H\end{matrix}\right\}O\end{matrix}$	$\begin{matrix}\left.\begin{matrix}H^2\\(C^2O^2)''\end{matrix}\right\}N\\ \left.\begin{matrix}H\end{matrix}\right\}O\end{matrix}$

The same compound may, in many cases, be referred to different types. Thus trichloride of phosphorus, PCl^3, may be derived, either from a triple molecule of hydrochloric acid, 3HCl, by substitution of P''' for H^3; or from ammonia, NH^3, by substitution of P for N, and of Cl^3 for H^3. In the same manner, the typical molecule, NH^3, itself may be regarded as three molecules of hydrogen, 3HH, held together by the substitution of N''' for H^3; and the typical molecule of water, H^2O, may also be regarded as two molecules of hydrogen, H^2H^2, held together by the diatomic element, O.

It appears, then, that the different types may also be reduced to one, namely hydrogen, which may therefore be regarded as the representative of the smallest molecular unity, or as the unit of molecule. In other words, all chemical compounds may be regarded as aggregations of ideal hydrogen-molecules, held together by the introduction of one or more polyatomic elements or radicles.

"The reduction of the typical mode of representation to this last consequence, shows plainly that the entire system is nothing more than a comparison of compounds with regard to their composition, not a true theory which can teach us anything about their actual composition itself. The several types are, therefore, not classes of compounds distinctly separated from one another by difference of constitution, but rather movable groups, in which compounds may be placed together, according to the particular analogies which it is desired to bring to light." (Kekulé.)

TYPHA. Two species of this water-plant have been chemically investigated. The pollen of *T. latifolia* contains, according to Braconnot (Ann. Ch. Phys. [2], xlii. 919), 3·6 per cent. stearin and olein, 18·3 sugar, 2·0 starch, 25·9 pollenin, 2·5 magnesium- and potassium-phosphates, together with small quantities of other potassium-salts, and 0·4 silica.

The rootstock of the same plant contains, in the fresh state, according to Lecocq (J. Chim. méd. xlii. 91), in December, 12·5 pts. starch to 73 pts. water; but in April, only 10·5 pts. starch to the same quantity of water. A decoction of the root is said to be used in Turkey as a remedy for dropsy and for snake-bites. (Landerer.)

100 pts. of the entire plant of *Typha angustifolia* contain, after drying, 9·58 per cent. ash; and the ash contains, in 100 pts., 14·8 K^2O, 21·9 CaO, 1·56 MgO, 0·2 Fe^2O^3, 2·5 SO^3, 0·6 SiO^2, 21·0 CO^2, 3·9 P^2O^5, 16·8 KCl, and 16·9 NaCl. (Schulz-Fleeth, Pogg. Ann. cxv. 157.)

TYRITE. See NIOBATES OF YTTRIUM (iv. 55).

TYROLITE. *Copper-froth. Pharmacosiderite. Cupriferous Calamine. Kupaphrite. Kupferschaum.*—A basic arsenate of copper, $\breve{Cu}^3As^2O^8.2Cu''H^2O^2.7H^2O$, or $5Cu''O.As^2O^5.9H^2O$, found native at Falkenstein in the Tyrol, and in other localities, sometimes in trimetric crystals, with the faces $oP \,.\, \infty\breve{P}\infty \,.\, \infty P$, cleaving perfectly parallel to oP; more frequently reniform, massive; structure radiate, foliaceous; surface drusy. Specific gravity = 3·02 to 3·098. Hardness = 1—2. Lustre, pearly on the face oP, vitreous on the other faces. Colour apple-green and verdigris-green, inclining to skyblue. Streak a little paler. Translucent to subtranslucent. Fracture not observable. Very sextile. Thin laminæ flexible. Decrepitates strongly when heated; melts before the blowpipe to a noncrystalline bead, colouring the flame green. On charcoal it emits moisture quietly, and on long exposure to the blowpipe-flame swells a little from escape of arsenic-vapour. With soda it forms an imperfectly fluid mass, containing a white metallic nucleus. Dissolves in acids, with evolution of carbonic acid.

Kobell's analysis (Pogg. Ann. xviii. 253) gave 25·01 per cent. As^2O^5, 43·88 CuO, 17·46 water, and 13·65 carbonate of calcium; or, abstracting the latter, 28·96 per cent. As^2O^5, 50·82 CuO, and 20·22 water, the formula $5Cu^2O.As^2O^5 + 9H^2O$ requiring 29·20 Cu^2O, 50·28 As^2O^5, and 20·52 water.

Copper-froth occurs in the cavities of calamine, calcspar, or quartz, together with other ores of copper, in small aggregated and diverging fibrous groups, having a pale-green colour and delicate silky lustre. (Dana, ii. 426; Rammelsberg, p. 378.)

TYROSINE. $C^9H^{11}NO^3$. (Liebig, [1846], Ann. Ch. Pharm. lvii. 127; lxii. 269.—Warren De la Rue, *ibid.* lxiv. 35.—Bopp, *ibid.* lxix. 20.—Hinterberger, *ibid.* lxii. 72.—Strecker, *ibid.* lxxiii. 70.—Piria, *ibid.* lxxxii. 251.—Alex. Müller, J. pr. Chem. lvii. 162.—Leyer and Köller, Ann. Ch. Pharm. lxxxiii. 332.—Wittstein, Jahresb. 1854, p. 656.—Frerichs and Städeler, *ibid.* 1855, p. 729; 1856, p. 702.—R. Hoffmann, Ann. Ch. Pharm. lxxxvii. 123.—Städeler, *ibid.* cxi. 12; cxv. 57.—Erlenmeyer and Schöffer, Jahresb. 1859, p. 596.—Neubauer, Ann. Ch. Pharm. cvi. 72.—Fröhde, Jahresb. 1860, p. 579.—Schmeisser, Arch. Pharm. [2], c. 14.—Kölliker and H. Müller, Ber. d. phys. Anat. zu Würzburg, vii. 3.—Schmetzer, *Inaugural Dissertation*, Erlangen, 1862.—Gorup-Besanez, Ann. Ch. Pharm. xcviii. 13; cxxv. 381.—Scherer, J. pr. Chem. lxx. 406.—C. Wicke, Ann. Ch. Pharm. ci. 314.—R. Schmitt and O. Nasse, *ibid.* cxxxiii. 211.—L. Barth, *ibid.* cxxxvi. 110; Bull. Soc. Chim. 1866, i. 307.—G. Beyer, Zeitschr. f. Chem. [2], iii. 436; Bull. Soc. Chim. 1867, ii. 368.)

A crystalline nitrogenous body, produced by the decomposition of albuminoïdal substances under the influence of acids, alkalis, and putrefaction. It was discovered by Liebig, who obtained it by decomposing casein with melting potash. A. Müller found it amongst the products of the putrefaction of yeast. Leyer and Köller obtained it by the action of fused potash on globulin, feathers, hairs, and hedgehog's prickles, or by treating these bodies with sulphuric acid. Hinterberger prepared it by boiling ox-horn with sulphuric acid. Städeler obtained it in like manner from muscle-fibrin, vegetable fibrin, fibroin, and animal mucus. Städeler has further pointed out that the white bodies, resembling poppy-seeds, sometimes observed in badly-preserved alcoholic anatomical preparations, also consist of tyrosine; and that the so-called cystinoïd tubercles, or xanthocystin, found by Chevallier and Lassaigne on a corpse two months old, likewise agreed in character with this substance.

Tyrosine occurs ready-formed, and always accompanied by leucine, in the animal organism: it has been found in the spleen, and the pancreas; in the liver and in the blood of the hepatic veins, in certain states of liver-disease; in the bile of typhous patients; and in the urine, sometimes forming crystalline sediments (Frerichs and Städeler); in the cutaneous scales in pellagra (Schmetzer). It occurs also in cochineal (De la Rue), probably as a product of decomposition, and in most of the lower forms of animal life. According to Wittstein, it is found in American extract of rhatany.

Preparation.—From Casein.—Well-pressed cheese, prepared from milk, either fresh or curdled, and freed as much as possible from adhering butter, is fused with its own weight of potassium-hydrate (or with solution of potash strong enough to crystallise on cooling) until hydrogen, as well as ammonia, is evolved from the melting mass; the mass is dissolved in hot water, and slightly supersaturated with acetic acid; and the filtered liquid is left to cool, whereupon needles of tyrosine separate, which are purified by repeated solution in water containing potassium-carbonate, and precipitation with acetic acid (Liebig). To purify it from leucine, when obtained in this manner, or according to preparation 5 of leucine (iii. 580), it is recrystallised from hot, and then washed with cold water. It still retains some brown-red matter, to remove which the solution in hydrochloric acid is treated with animal charcoal, decomposed with a quantity of potassium-acetate equivalent to the amount of hydrochloric acid, and rapidly filtered, whereupon the filtrate becomes filled with entangled needles. A portion of the tyrosine remains dissolved in the acetic acid, but the rest is thereby freed from ash, which adheres obstinately to the tyrosine crystallised from neutral solutions. The needles are washed with cold water, and once more crystallised. (Bopp.)

From Horn.—Dilute sulphuric acid (1 pt. oil of vitriol to 4 pts. water) is boiled in a copper vessel with horn-shavings (equal to half the weight of the oil of vitriol) for about twelve hours, renewing the water as it evaporates. The liquid is then diluted with water, mixed with milk of lime to alkaline reaction, and strained; the residue is exhausted with hot water; the liquid evaporated at the boiling heat to about two-thirds the volume of the dilute sulphuric acid, and then neutralised with sulphuric acid; the impure tyrosine, which separates in twenty-four hours, is collected; and an additional quantity is obtained by evaporating the mother-liquor, together with leucine, which must be separated by solution in cold water. The impure tyrosine is next heated with dilute soda-ley; and the tyrosine which separates after twelve hours is again collected, and further purified by recrystallisation from aqueous ammonia. Horn-shavings treated in this manner yield, on the average, 4 per cent. tyrosine and 8 per cent. leucine; fibroïn (silk) and animal mucus more than 4 per cent. tyrosine (Städeler). For Erlenmeyer and Schöffer's determinations of the quantities of tyrosine and leucine obtained by boiling various animal substances with dilute sulphuric acid, see LEUCINE (iii. 579).

Tyrosine, even after repeated crystallisation from aqueous ammonia, is often contaminated with a small quantity of a sulphurous compound, which adheres obstinately to it. To remove this impurity, Städeler dissolves the tyrosine in water, mixes the warm solution with a small quantity of basic lead-acetate, and removes the lead from the clear filtrate by sulphuretted hydrogen. The concentrated solution then yields, by evaporation, perfectly pure tyrosine.

From Cochineal.—Decoction of cochineal is precipitated by neutral acetate or basic nitrate of lead; the liquid is filtered from the carminate of lead, and treated with sulphuretted hydrogen; and the filtrate is evaporated to a syrup, whereupon a chalk-like substance separates. This is washed with cold water, and several times recrystallised from boiling water, ultimately with the aid of animal charcoal. The separated crystals, which have a silky lustre, shrink on the filter to a paper-like mass also having a silky lustre. 300 parts of cochineal yield 1 pt. of tyrosine. (De la Rue.)

Properties.—Tyrosine crystallises from aqueous solution in stellate groups of long slender needles, having a silky lustre, and becoming interlaced and confused in drying. From ammoniacal solutions, it crystallises in permanent tufts of larger needles, also having a silky lustre; and by supersaturating warm dilute hydrochloric acid with tyrosine, a crop of crystals is obtained, consisting of rather thick oblong prisms, with a horizontal dome resting on the narrow sides.

Tyrosine dissolves in 150 pts. of boiling *water*, in 1900 pts. of cold water (at about 16°), in about 13,500 pts. of cold 90 per cent. *alcohol*, not much more freely in boiling alcohol, and is quite insoluble in *ether*. Its solubility in alcohol is greatly increased by admixture with amorphous extractive matter.

Tyrosine-solutions are not precipitated either by *neutral* or by *basic acetate of lead*; but on addition of ammonia, the basic acetate produces a precipitate consisting of tyrosine combined with lead. A solution of tyrosine is not altered by addition of *mercuric acetate*, unless previously mixed with basic acetate of lead; in which case the tyrosine is almost completely precipitated as a mercury-compound, from which it may be separated by sulphuretted hydrogen. An aqueous solution of tyrosine mixed with *mercuric nitrate* remains clear; but on adding a small quantity of soda, a white precipitate is formed, containing tyrosine, mercuric oxide, and nitric acid. A moderately dilute solution of tyrosine boiled with mercuric nitrate, turns red and deposits a brown-red precipitate. Very dilute solutions assume a faint rose-colour, and yield a yellow or flesh-coloured precipitate (R. Hoffmann; Städeler). A small quantity of tyrosine gently warmed with a few drops of strong *sulphuric acid* yields, after dilution with water and neutralisation with barium-carbonate, a liquid which is coloured violet by *ferric chloride*; this reaction affords a very delicate test for tyrosine. (Piria; Städeler.)

Tyrosine heated for some time with *chlorine*, or *bromine*, is converted into perchloroquinone, or perbromoquinone; at ordinary temperatures, on the other hand, bromine forms dibromotyrosine. When chlorate of potassium is added to the hydrochloric acid solution of tyrosine, a wine-red coloration is produced; oily drops separate; and the liquid when distilled yields chlorinated acetone, leaving a resinous mass, which, by the further action of hydrochloric acid and potassium-chlorate, is converted into perchloroquinone.

Tyrosine heated with dilute sulphuric acid and *peroxide of lead* is completely decomposed, carbonic anhydride being slowly evolved, and the brown liquid, when freed from sulphuric acid by means of barium-carbonate, yielding, on addition of alcohol, a dark-coloured precipitate, while the filtrate on slow evaporation deposits a few small crystals.—Alkaline tyrosine-compounds decompose *permanganate of potassium* even in the cold, forming oxalic acid and a brown substance (Neubauer). Tyrosine distilled with *potassium-chromate* and sulphuric acid, yields bitter-almond-oil, hydrocyanic acid, benzoic acid, formic acid, acetic acid, and carbonic acid. (Fröhde.)

Tyrosine heated with *nitric acid*, yields nitro-substitution-products.

Tyrosine is decomposed by *heat*, emitting an odour of burnt horn; when heated in considerable quantity (mixed with pumice-stone), it yields an oily distillate, smelling strongly of phenol (Städeler). But when very small quantities of it are heated in thin glass tubes to about 270°, a white alkaline sublimate, $C^8H^{11}NO$, is obtained, very slightly soluble in water, and forming a crystallisable hydrochlorate and chloroplatinate. This body has the composition of ethyl-oxyphenylamine, $C^6H^6(C^2H^5)NO$, and accordingly tyrosine, from which it is formed by elimination of carbonic anhydride, may be regarded as ethyl-amidosalicylic acid:

$$\underset{\text{Amidosalicylic acid.}}{C^7H^7NO^3} = \underset{\text{Oxyphenylamine.}}{C^6H^7NO} + CO^2.$$

$$\underset{\text{Ethyl-amidosalicylic acid.}}{C^7H^6(C^2H^5)NO^3} = \underset{\text{Ethyl-oxyphenylamine.}}{C^6H^6(C^2H^5)NO} + CO^2.$$

(Schmitt and Nasse, Ann. Ch. Pharm. cxxxiii. 211.) On the other hand, according to L. Barth (*ibid.* cxxxvii. 110), tyrosine, fused with caustic potash, is resolved into paraoxybenzoic acid, acetic acid, and ammonia, as shown by the equation:

$$\underset{\text{Tyrosine.}}{C^9H^{11}NO^3} + H^2O + O = \underset{\text{Paraoxy benzoic acid.}}{C^7H^6O^3} + \underset{\text{Acetic acid.}}{C^2H^4O^2} + NH^3;$$

and may, accordingly, be regarded as the ethylic derivative of amidoparaoxybenzoic acid:

$$\underset{\text{Amidoparaoxybenzoic acid.}}{C^7H^5(NH^2)O^3} \qquad \underset{\text{Tyrosine.}}{C^7H^5(NH.C^2H^5)O^3}.$$

Compounds of Tyrosine.—Tyrosine dissolves in *acids* and in *alkalis*, forming definite compounds. It unites with acids in two proportions, but is not capable of neutralising them. It has rather the properties of a weak acid, decomposing the carbonates of the alkaline earth-metals at the boiling heat, and forming, partly amorphous, partly crystalline compounds, which have a somewhat strong alkaline reaction.

Tyrosine dissolves abundantly in *ammonia*, but crystallises out from the solution unaltered. With the fixed bases, on the contrary, it easily forms definite compounds.

The *barium-compound*, $C^9H^9Ba''NO^3.2H^2O$, forms somewhat sparingly soluble prismatic crystals, more soluble in cold than in hot water. The aqueous solution has an alkaline reaction, and is precipitated by alcohol.—There appears to be also a compound containing $C^9H^9Ba''NO^3.C^9H^{11}NO^3$.—The *calcium-salt*, $C^9H^9Ca''NO^3$, prepared by dissolving tyrosine in lime-water, does not crystallise. A solution of tyrosine boiled with calcium-carbonate, appears to yield a mixture of this salt with the compound $C^9H^9Ca''NO^3.C^9H^{11}NO^3$.—The *sodium-salt*, $C^9H^9Na^2NO^3$, is formed by saturating dilute soda-ley with tyrosine. The solution is alkaline, and is not precipitated by alcohol.

Silver-salts.—On adding a saturated ammoniacal solution of tyrosine, by drops and with constant stirring, to a concentrated solution of silver-nitrate, in such quantity that the liquid no longer smells of ammonia, a heavy amorphous precipitate is formed, containing $C^9H^9Ag^2NO^3.H^2O$. After a certain quantity of the ammoniacal solution has been added, no further precipitation takes place; but if the liquid be then neutralised with nitric acid, the compound $2C^9H^{10}AgNO^3.H^2O$, separates as a heavy crystalline powder. Both compounds are slightly soluble in water, but turn red litmus-paper blue. They dissolve easily in nitric acid and in ammonia, and are decomposed by boiling with water.

Hydrochlorate of Tyrosine, $C^9H^{11}NO^3.HCl$, separates in needle-shaped crystals, on adding an excess of strong hydrochloric acid to a solution of tyrosine in the same acid. Water and dilute alcohol decompose it immediately into tyrosine and hydrochloric acid; but absolute alcohol dissolves it without decomposition, forming a solution which is not precipitated by platinic chloride; the salt is insoluble in ether.

Nitrate.—Tyrosine, triturated to a paste with water, remains colourless when nitric acid is added to it, not in excess; and the liquid filtered from undissolved tyrosine, yields, by spontaneous evaporation, radiate groups of needles, probably consisting of the salt $C^9H^{11}NO^3.HNO^3$.

The *sulphate*, $C^9H^{11}NO^3.H^2SO^4$, is obtained, by treating tyrosine in excess with dilute sulphuric acid, and leaving the filtrate to evaporate, in long slender needles, which are not coloured by ferric chloride, suffer no loss of weight at 115°, and dissolve easily in water; the aqueous solution, however, soon deposits tyrosine.

No compounds of tyrosine with organic acids have yet been obtained.

Derivatives of Tyrosine.

Amidotyrosine, $C^9H^{12}N^2O^3 = C^9H^{10}(NH^2)NO^3$. (G. Beyer, Bull. Soc. Chim. 1867, ii. 369.)—Obtained by reducing nitrotyrosine with tin in presence of dilute hydrochloric acid. The solution, freed from tin by sulphuretted hydrogen, and quickly evaporated (any brown colour that may appear being removed from time to time by sulphuretted hydrogen), yields nearly colourless hydrochlorate of amidotyrosine. To obtain the base, the aqueous solution of this salt is mixed with soda, not in excess, and evaporated to 100°, till it concretes into a thick magma, a resinous matter which forms during the evaporation being previously removed by filtration. The crystalline magma is then left to cool in a vacuum, and freed by pressure from chloride of sodium, which remains in solution.

Amidotyrosine thus prepared is an anhydrous crystalline powder, very soluble in water, slightly soluble in alcohol, permanent in the air when dry, but easily absorbing moisture, and then turning brown. Heated above 100°, it decomposes, and yields by distillation an oleaginous liquid, which solidifies to a crystalline mass on cooling.

Amidotyrosine forms well-crystallised salts.—The *hydrochlorate*, $C^9H^{12}N^2O^3.2HCl.H^2O$, crystallises in long needles, and sometimes forms a white hygroscopic powder. It gives off its water at 120°, without coloration. The aqueous solution quickly acquires a violet-brown colour. It is more soluble in alcohol than the free base. The solution at the boiling heat quickly reduces silver-oxide and platinic chloride to the metallic state, a resin soluble in ammonia being formed at the same time.—The *acid sulphate*, $C^9H^{12}N^2O^3.2H^2SO^4$, separates on cooling in anhydrous nodules, soluble in water, when the hydrochlorate is evaporated over the water-bath with dilute sulphuric acid.—The *neutral sulphate*, $C^9H^{12}N^2O^3.H^2SO^4$, is formed on adding the free base to an equivalent quantity of the acid salt in concentrated solution, and separates in well-defined crystals; it reduces oxide of silver.—*Sulphate of zinc and amidotyrosine*, $ZnSO^4.2(C^9H^{12}N^2O^3.H^2SO^4)$, is obtained in the crystalline state from a mixture of the two sulphates.

Dibromotyrosine, $C^9H^9Br^2NO^3.2H^2O$. (Gorup-Besanez.)—The hydrobromate of this base, produced by the action of bromine-vapour on excess of tyrosine, splits up, when boiled with water, into hydrobromic acid and dibromotyrosine. The base separates from concentrated solutions, in slender white needles; from more dilute solutions, after some time, in fan-shaped groups of large rhomboïdal tables, or in thick prismatic crystals belonging to the triclinic system. The crystals are, at first, perfectly transparent, but, when exposed to the air, gradually give off their water of crystallisation, and become milkwhite. Dibromotyrosine is more soluble in hot than in cold water, sparingly soluble in alcohol, insoluble in ether; has a slightly bitter taste, an acid reaction, and gives off the whole of its crystallisation-water at 100°. At a higher temperature it decomposes, giving off an odour like that of phenyl-compounds. It dissolves in alkalis, with decomposition, and formation of metallic bromide; and when treated with nitric acid, immediately becomes reddish, gives off bromine, and forms a solution, which, on evaporation, gradually deposits crystals of dinitrotyrosine.

Dibromotyrosine unites with acids and with bases, forming compounds which may be prepared similarly to those of tyrcsine itself.—The *silver-compound*, $C^9H^7Br^2Ag^2NO^3$, is a white crystalline precipitate, which turns brown on exposure to light, is decomposed by boiling with water, also by nitric acid, which separates bromide of silver.

Hydrobromate of Dibromotyrosine, $C^9H^9Br^2NO^3.HBr$, crystallises in stellate groups of small nacreous needles, easily soluble in water and in alcohol, but decomposed by boiling with water.—The *hydrochlorate*, $C^9H^9Br^2NO^3.HCl\,.\,\frac{3}{2}H^2O$, gives off its water of crystallisation at 100°, and in other respects resembles the hydrobromate.—The *sulphate*, $(C^9H^9Br^2NO^3)^2.H^2SO^4$, forms interlaced needles, easily soluble in water and in alcohol.

Nitrotyrosine, $C^9H^{10}(NO^2)NO^3$. (Strecker, Ann. Ch. Pharm. lxxiii. 70.)—When tyrosine is suspended in four times its bulk of water, and a quantity of nitric acid of specific gravity 1·3, equal in volume to the water, is gradually added, the solution becomes warm, acquires a red colour, and, after standing for twelve hours in a warm place, deposits an abundant crystallisation of nitrate of nitrotyrosine; and on pressing these crystals between paper, dissolving them in water, and adding as much ammonia as can be added without reddening, nitrotyrosine is deposited: it may also be separated from the solutions of its salts by acetate of ammonium.

Nitrotyrosine forms delicate yellow needles, united in warty groups, or in beautiful wavellitic crystalline geodes. It is slightly soluble in cold, more soluble in hot water, insoluble in alcohol and ether, has a slightly bitter taste, reddens litmus, and decomposes with slight detonation when heated above 100°. It dissolves in ammonia, the fixed alkalis, and dilute mineral acids, but not in acetic acid.

Nitrotyrosine unites with acids and with bases, in the same manner as tyrosine.—The *barium-salt*, $Ba''[C^9H^9(NO^2)NO^3]^2$, is a blood-red amorphous mass.—The *silver-salt*, $C^9H^8Ag^2(NO^2)NO^3$, is an orange-yellow precipitate, soon changing to a deep red granular powder, somewhat soluble in water; there appears also to be another silver-compound containing $C^9H^9Ag(NO^2)NO^3$.

Hydrochlorate of Nitrotyrosine, $2[C^9H^{10}(NO^2)NO^3.HCl].H^2O$, crystallises in tufts of lemon-yellow needles, easily soluble in water and in alcohol.—The *nitrate*, $C^9H^{10}(NO^2)NO^3.HNO^3$, forms lemon-yellow needles, insoluble in ether, easily soluble in alcohol, soluble in 5 pts. of water; the solution decomposes on standing, depositing nitrotyrosine.—*Sulphate of Nitrotyrosine*, $2C^9H^{10}(NO^2)NO^3.H^2SO^4$, forms yellow needles or granules.

Dinitrotyrosine, $C^9H^9(NO^2)^2NO^3$. (Städeler, Jahresb. 1860, p. 576.)—Produced by gently heating nitrate of nitrotyrosine with a mixture of equal volumes of water and nitric acid of specific gravity 1·3. On washing the lemon-yellow residue with cold water, and recrystallising it from boiling water, the dinitrotyrosine is obtained in golden-yellow shining laminæ. It is very slightly soluble in cold water, not much more in hot water, easily soluble in alcohol, less soluble in ether; has a slight acid taste; makes a deep yellow stain; melts at 115°, and decomposes with slight detonation.

Dinitrotyrosine unites easily with metals, forming red and yellow salts, which detonate violently when heated.—The *ammonium-salt* crystallises from an aqueous solution mixed with alcohol and ether, in stellate groups of needles, having a deep chrome-red colour with violet reflex.—The *barium-salt*, $C^9H^7Ba''(NO^2)^2NO^3.2H^2O$, crystallises in rather thick ruby-coloured prisms, more soluble than the calcium-salt.—The *calcium-salt*, $C^9H^7Ca''(NO^2)^2.NO^3.3H^2O$, is precipitated in golden-yellow six-sided tables, on adding ammonia to a solution of dinitrotyrosine mixed with chloride of calcium: it is insoluble in alcohol and ether, slightly soluble in water, more readily in dilute acetic acid.—The *lead-salt* separates, on mixing a solution of dinitrotyrosine with acetate of lead, in orange-coloured flocks, which, if left in the liquid, gradually become crystalline, and are converted into large stars, formed of chrome-red hexagonal tables.—The *magnesium-salt* crystallises in stellate tufts of very delicate bright-red needles.—The *silver-salt* is precipitated by ammonia, from a solution of dinitrotyrosine mixed with silver-nitrate, in red flocks, which soon become crystalline.

Erythrosin.—This name is given by Städeler to the red colouring-matter, formed when tyrosine is dissolved in excess of nitric acid, or when a solution of tyrosine-nitrate is left to evaporate in the air, and probably also by the action of ozone on tyrosine (Gorup-Besanez). It is a red-brown substance, insoluble in the ordinary solvents, but easily soluble in alcohol containing sulphuric acid, from which solution it is partly precipitated by ammonia, the remaining liquid being green by transmitted, red and opaque by reflected light. Erythrosin dissolves in the fixed alkalis with brown-red or violet colour, in strong sulphuric acid also with violet colour. Städeler thinks it not improbable that this body may be identical with hæmatoïdin.

TYROSINE-SULPHURIC ACID. (Frerichs and Städeler, Jahresb. 1854, p. 675.—Städeler, Ann. Ch. Pharm. cxvi. 57; Jahresb. 1860, p. 577.)—Tyrosine forms, with sulphuric acid, several acids containing the radicle SO^2.—α. On heating it to 100°, with four or five times its weight of strong sulphuric acid, a monobasic acid, $C^9H^{11}NO^3.SO^3$, is formed, which, on diluting with water, neutralising with carbonate of barium, and decomposing the filtrate with sulphuric acid, is partly precipitated, together with the barium-sulphate, as anhydrous crystalline acid, and partly separates, on evaporating the mother-liquor, as hydrated pulverulent acid, $C^9H^{11}NO^3.SO^3.2H^2O$.

The crystalline acid is very slightly soluble in cold water, dissolves slowly in hot water, and is gradually deposited from this solution, on evaporation, or on addition of hydrochloric or nitric acid, in prisms or tables; it is but very slightly soluble in alcohol, even at the boiling heat.—The hydrated acid is a starchlike powder, containing from 0·8 to 12 per cent. water, and much more soluble in water and alcohol than the crystalline acids (12 per cent. water = 2 at.).

Tyrosine-sulphuric acid has a strong acid reaction, and produces, with a small quantity of ferric chloride, a splendid violet colour—or rose-red in very dilute solutions. Its salts, which are mostly very soluble, and likewise produce the violet colour with ferric chloride, are amorphous, and not precipitable by nitrate of silver or neutral acetate of lead, but yield a precipitate with the basic acetate.—The *ammonium-salt*, $C^9H^{10}(NH^4)NO^3.SO^3.H^2O$, gives off water and ammonia when heated, and then becomes acid.—The *barium-salt*, $C^9H^{10}Ba''NO^3.SO^3.2H^2O$, and the *calcium-salt*, $C^9H^{10}Ca''NO^3.SO^3.2\frac{1}{2}H^2O$, have an alkaline reaction, and disagreeable saline bitter taste.

β. When tyrosine and sulphuric acid are heated in the proportions above mentioned, but more strongly and for a longer time, an acid is formed, the barium-salt of which has the same composition as the above, but a neutral reaction and sweet taste.

γ. By strongly heating tyrosine with 8 to 12 pts. sulphuric acid, dibasic acids are produced, the barium-salts of which still yield the violet colour with ferric chloride, but differ in composition and in their other properties from those above described. One of these barium-salts, crystallised in nodules, was tasteless, had an alkaline reaction, dissolved slightly in cold, more freely in hot water, and was found to consist of $C^9H^9Ba''NO^3.SO^3.3H^2O$.

δ. The action of sulphuric acid on tyrosine at high temperatures appears also to yield other acids, resulting from more advanced decomposition: they all give the violet colour with ferric chloride, but have not been further examined. (Städeler.)

U

UIGITE. A mineral from Uig, in the Isle of Skye, containing 52·40 per cent. silica, 17·98 alumina, 9·97 lime, 0·36 magnesia, 0·03 potash, 1·40 soda, and 17·83 water. It has a white to light-yellow colour, nacreous lustre, hardness = 5·5, and specific gravity = 2·284. Before the blowpipe it melts quietly and easily to an opaque enamel. (Heddle, N. Jahrb. f. Mineral. 1858, p. 823.)

ULEXITE. Syn. with BOROCALCITE (i. 643).

ULLICO. Attempts have been made in Holland to cultivate the root of *Ullico tuberosus* on the large scale as a substitute for the potato. 100 pts. of the fresh root contain 87·9 pts. water, 10·95 organic matter, and 1·15 ash. 100 pts. of the dry substance contain 3·1 pts. fat (mostly crystallisable), 29·4 fruit-sugar (with extractive matter and a little resin), 4·0 gum, 33·3 starch, 11·9 solid albumin, 18·3 cellulose, and other insoluble substances. The dry root contains 2·6 per cent. nitrogen, equivalent to 17 per cent. albuminous substance. The ash contains lime, ferric oxide, soda, sulphuric acid, phosphoric acid in large quantity, chlorine, and carbonic acids, together with small quantities of magnesia, potash, and silica. (**Mulder** and **Schablée**, Pharm. Centr. 1851, p. 269.)

ULLMANITE. Antimonial or antimonio-arsenical nickel-glance, $NiS.Ni(Sb;As)^2$ (iv. 43).

ULMARIC ACID. Buchner's name for spiræic or salicylous acid, obtained from *Spiræa ulmaria.*

ULMIC ACID. ULMIN. See the next article.

ULMOUS or **HUMOUS SUBSTANCES.** These names are given to various brown or black substances, occurring in vegetable mould, peat, stable-manure, dung-water, and certain mineral waters, and resulting from the putrefaction of vegetable or animal substances in contact with air and water. Similar substances are produced by the action of acids and alkalis on cellulose, starch, sugar, fibrin, albumin, &c.; but the composition of these products appears to vary according to the circumstances under which they are formed, and the nature of the reagents used in preparing them.

When sugar is boiled for some time with dilute hydrochloric, nitric, or sulphuric acid, black or brown scales are deposited, which, after being washed with water, dissolve partially in ammonia, leaving a black insoluble substance called ulmin; and the ammoniacal solution, when neutralised with an acid, deposits brown or black gelatinous flocks of ulmic acid, soluble in pure water, but insoluble in water containing free acid or sulphate of potassium. Ulmic acid and ulmin have the same composition, $C^{24}H^{18}O^9$, according to Stein (Ann. Ch. Pharm. xxx. 84), differing from that of sugar only by the elements of water. Ulmic acid is converted into ulmin by prolonged desiccation, and more quickly by boiling with strong hydrochloric acid.

When vegetable mould, or mouldered wood from the trunk of a decaying tree, is digested in a weak solution of potash or soda, a brown liquid is formed, which, on addition of an acid, yields a blackish-brown precipitate, easily soluble in alkalis, and always retaining a considerable proportion of nitrogen. Mulder (Ann. Ch. Pharm. xxxvi. 243) regards this precipitate as a mixture of three substances, which are compounds of water, or of water and ammonia, with three different acids, viz.—geic acid, $C^{20}H^{12}O^7$; humic acid, $C^{20}H^{12}O^6$; and ulmic acid, $C^{20}H^{14}O^6$. These formulæ are very doubtful, but the substances in question are obviously the product of vegetable matter in a state of decay more or less advanced. They are very much like the above-mentioned products of the decomposition of sugar.

The name "ulmic acid," or "ulmin," was given by Klaproth to a gummy substance contained in the black alkaline excrescences on the stems of unhealthy trees, especially of elms.

Ulmin is also the name of a brown pigment, produced by the action of strong acids or alkalis on various organic bodies, especially by heating treacle or alcohol with strong sulphuric acid, thoroughly washing the residue with water, then triturating it with gum, and drying the mixture. A similar colour is obtained by boiling alcohol with solid caustic potash, washing the product with hydrochloric acid, and then with water.

For details respecting the various observations which have been made upon ulmous or humous substances, see *Gmelin's Handbook*, xvii. 458.

ULMUS. The bark of the common elm, *Ulmus campestris*, contains tannin, resin, mucus, and inorganic salts; the mucus, according to Braconnot, is very much like that of linseed. The bark of old elms often exudes gummy or mouldy substances, containing vegetable mucus, together with the carbonates of potassium, calcium, and magnesium. Klaproth's ulmin was a substance of this kind. The leaves of the elm are said to contain a bitter principle and a yellow colouring-matter, and (according to Kellerman) the flowers, at the time when the buds turn red, contain a red and a green colouring-matter.

The composition of the ash of the bark and wood is as follows:—

	K^2O.	Na^2O.	CaO.	MgO.	$Fe'''PO^4$.	P^2O^5.	SO^3.	SiO^2.	
Bark	2·2	10·1	72·7	3·2	1·2	1·2	0·6	8·8	= 100
Wood	21·9	13·7	47·8	7·7	1·7	2·8	1·3	3·1	= 100

ULTENITE. A rock occurring in the Ulten Valley in the Tyrol, consisting of a crystalline, fine-grained, slaty mixture of garnet with disthene and a small quantity of mica.

ULTRAMARINE. *Outremer.*—The fine blue pigment known by this name consists essentially of silica, alumina, soda, and sulphur, and is regarded as a sodio-aluminic silicate, united either with polysulphide of sodium alone, or with a polysulphide and a polythionate of sodium.

Ultramarine occurs native in several minerals, to which it imparts its blue colour, and the characteristic property of giving off sulphydric acid and yielding a jelly of silica, when treated with hydrochloric acid; such are nosean, hauyne, ittnerite, and especially lapis-lazuli, which occurs intergrown with limestone, and mixed with iron-pyrites, in Siberia, Thibet, China, and on the Cordillera of Ovalle in South America. From this mineral, ultramarine was formerly obtained by gently calcining the stone, broken into fragments of about the size of hazelnuts; quenching the heated fragments in vinegar, by which they were rendered more friable and were deprived of adhering carbonate of calcium;—then pulverising them; levigating the powder for a long time with a thin syrup of honey and dragon's-blood; mixing it to a paste with a resinous cement composed of colophony, white pitch, yellow wax, and linseed-oil; then leaving it at rest for some days; and extracting the ultramarine from it by suspension in water, and decantation. By this protracted mechanical treatment, the ultramarine was obtained in the form of a very fine soft powder, of various shades of blue, the portions first deposited being the darkest, and the last constituting a pale-blue powder called ultramarine ash (*cendres d'outremer*).

This process being very tedious, and the lapis-lazuli being a rare mineral, obtainable only from remote and difficultly accessible localities, natural ultramarine was necessarily a very costly article; and of late years, it has been entirely superseded by artificial ultramarine, which can be made equal, or even superior, to the natural product in colour and lustre, and at a price low enough to admit of its extensive use as a pigment.

The idea of preparing ultramarine artificially was suggested by the discovery of blue masses, more or less resembling it, on taking down soda-furnaces and limekilns. Tessaert, in 1814, found a blue mass of this kind in a soda-furnace at St. Gobain, and gave it to Vauquelin for analysis, who pronounced it to be lapis-lazuli (Ann. Chim. lxxxix. 88). Kuhlmann found on the hearth of a salt-cake furnace, similar blue masses surrounded with very small brown-red crystals of sodium-sulphide (Dumas' *Traité de Chimie appliquée*, ii. 419.) A similar observation was made by Hermann in Schönebeck. These observations induced the *Société d'Encouragement* at Paris, in 1824, to offer a prize of 6,000 francs for the discovery of a mode of preparing ultramarine artificially; and this prize was awarded to Guimet, of Toulouse, in 1828. A mode of obtaining artificial ultramarine had, however, been previously discovered by Christian Gmelin, and published by him at the beginning of the year 1828 (Würtemberg Naturw. Abhandl. ii. 191). Guimet's process was first applied on the manufacturing scale, but it was kept secret. Gmelin's process is as follows:—

Soda-ley saturated with precipitated silica, is mixed with aluminium-hydrate (containing 20 per cent. water, and obtained by precipitation from alum not containing iron), in such proportion that the mixture shall contain 31 pts. dry silica to 26 pts. dry alumina; the liquid is then evaporated to dryness, and the pulverised residue is mixed with flowers of sulphur. In the next place, the same quantity of a mixture of dry sodium-sulphate and flowers of sulphur, in equal parts, is weighed out; the whole carefully mixed and stamped into a crucible, so as to fill it completely; the crucible, tightly closed, is quickly heated to redness, so that the sulphur may not volatilise before the sulphide of sodium can be formed; and the mass is kept at a red heat for two hours. The crucible is then left to cool with the cover on, and the greenish-yellow product (*green ultramarine*) is gently heated in porous crucibles, in which narrow channels have been bored to increase the draught. The blue mass thus obtained is finely pulverised, levigated, and washed.

Gmelin's process includes all the conditions essential to the preparation of a good ultramarine; all the more recent processes, indeed, differ from it, chiefly, in using clay instead of the artificially prepared mixture of silica and alumina. At the present day, manufacturers of ultramarine use mixtures of kaolin with Glauber-salt and charcoal, or with carbonate of soda and sulphur, or carbonate of soda and Glauber-salt together. The mixture is ignited in closed crucibles or boxes of fireclay; and the green ultramarine thus obtained is ground in a mill, and then roasted, with addition of sulphur, to convert it into blue ultramarine. Gentele (Dingl. pol. J. cxli. 116; cxlii. 350) gives the three following mixtures:

Kaolin, anhydrous	100	100	100
Calcined Glauber-salt	83 to 100	. .	41
Carbonate of soda	. .	100	41
Charcoal	17	12	17
Sulphur	. .	60	13

The colouring-matter of ultramarine has been made the subject of investigation by many chemists, but considerable doubt still exists as to its true nature. According to the experiments of Wilkens (Ann. Ch. Pharm. xcix. 21), who has made careful analyses of a variety of samples of artificial ultramarine, both from his own manufactory and from other sources, ultramarine is composed of two portions, one of which—regarded by him as the essential constituent—is constant in composition, and is attacked with facility by hydrochloric acid, evolving sulphuretted hydrogen; while the other portion, not soluble in hydrochloric acid, contains a variable amount of sand, clay, oxide of iron, and sulphuric acid. Wilkens's analyses of the pure blue pigment correspond nearly with the formula $(2Al^2O^3.3SiO^2).(Al^2O^3.4SiO^2).Na^2S^2O^3.3Na^2S$.

	Calculation.	Analyses.		
Silica	37·6	40·25	39·39	46·19
Aluminium . . .	27·4	26·62	26·40	25·85
Sulphur	14·2	13·42	12·69	13·27
Soda (Na^2O) . . .	20·0	19·89	21·52	20·69

Numerous other analyses are given in the *Handwörterbuch der Chemie* (ix. 19).

Wilkens regards the blue colouring-principle as a compound of hyposulphite and sulphide of sodium. He states that the presence of iron is not essential to the production of the colour, but about this there is still some doubt. According to Brunner, a corresponding compound, in which potassium-sulphide is substituted for sodium-sulphide, is colourless.

Ultramarine heated in the air, gradually assumes a dull green hue; it is not changed by heating with sulphur, but when melted with borax, gives off sulphur and sulphurous acid, and leaves a colourless glass. Sulphuric, nitric, and hydrochloric acids decompose it, quickly destroying the colour. Chlorine acts still more rapidly, dissolving everything but the silica, and completely discharging the colour.

Ultramarine is extensively used, not only as an artist's colour, but also for paper-staining and other forms of house-decoration, as well as in dyeing and calico-printing. In Germany, which is the chief seat of the ultramarine manufacture, there are about twenty factories, each producing annually about 1000 tons of the colour. The manufacture is also carried on in France and in Belgium, and to a smaller extent in England.

ULVA. The alga called *Ulva* or *Rivularea gelatinosa*, consists, according to Braconnot, of green globules and a colourless jelly; the latter is insoluble in water, at first, but dissolves on prolonged immersion. The solution resembles gum-water, but when treated with nitric acid, yields oxalic instead of mucic acid.

UMBELLIC ACID. This name was given by Persoz to a product of the oxidation of the volatile oil of anise, star-anise, and fennel with chromic acid. Hempel has, however, shown that the acid thus obtained is identical with anisic acid.

UMBELLIFERONE. $C^6H^4O^2$. (Sommer and Zwenger, Ann. Ch. Pharm. cxv. 15.—Mössmer, *ibid.* cxix. 260.)—A neutral body, isomeric or polymeric with quinone, to which, however, it exhibits no further resemblance. It is obtained by the dry distillation of various resins, chiefly of those derived from umbelliferous plants: thus crude galbanum yields, by dry distillation, 0·83 per cent. umbelliferone; sagapenum, 0·32 per cent.; *Asa fœtida*, 0·28 per cent. It is likewise obtained from opoponax, the resins of sumbul-root, angelica-root, *Radix levistici*, *R. meu*, and *R. imperatoriæ*. Gum-ammoniac does not yield it, but it may be obtained from the alcoholic extract of the bark of the mezereon or spurge-laurel (*Daphne mezereum*), a plant not belonging to the umbelliferous order.

Umbelliferone may be prepared from galbanum;—most advantageously, according to Mössmer, from the resin purified by boiling crude galbanum with water, dissolving the resinous residue in milk of lime, and precipitating the filtered solution with hydrochloric acid. By distilling this purified resin with water, an oily distillate is obtained, which, on standing, deposits crystals of umbelliferone, to be purified by recrystallisation. The distillate obtained from the alcoholic extract of mezereon-bark, contains daphnetin as well as umbelliferone. To separate the former, the solution of the purified crystals is mixed with acetate of lead, which throws down a compound of daphnetin with lead-oxide, while pure umbelliferone remains in solution, and crystallises on evaporation. Umbelliferone is likewise formed when a concentrated alcoholic solution of pure galbanum-resin, saturated with hydrochloric acid gas, is heated for some time to 100°.

Umbelliferone forms colourless rhombic prisms, having a faint silky lustre; it is tasteless, inodorous in the cold, dissolves slightly in cold water, and so abundantly in boiling water, that a solution, saturated while hot, coagulates, on cooling, to a crystalline pulp, forming, when dry, a coherent interlaced mass. Umbelliferone dissolves also in alcohol, ether, and chloroform. The aqueous solution is colourless by transmitted light, but exhibits, by reflected light, a splendid blue colour, which is deepened by addition of alkalis, but weakened or destroyed by acids.

Umbelliferone, when warmed (also its aqueous solution when boiled), emits an odour like that of coumarin. It melts, at 240°, to a yellowish liquid, which solidifies in the crystalline form on cooling; it sublimes below its melting-point, and volatilises without residue.

Umbelliferone does not appear to unite either with acids or with bases, and is not precipitated from its solutions by any salt except basic acetate of lead; the white precipitate thereby produced is decomposed by washing. Umbelliferone dissolves in most acids with aid of heat, not being decomposed even by strong sulphuric acid. Nitric acid converts it into oxalic acid. It reduces gold- and silver-salts, but does not appear to reduce an alkaline cupric solution.

Dibrom-umbelliferone, $C^6H^2Br^2O^2$, is produced by treating an alcoholic solution of umbelliferone with bromine, and separates in flocks, which may be purified by washing with water, then with dilute alcohol, and recrystallisation from alcohol. It is white and insoluble in water; its alcoholic solution exhibits a superficial light-green iridescence. (Mössmer.)

Dry umbelliferone is scarcely attacked by *chlorine*; but the aqueous solution, when treated with chlorine, is quickly decomposed, depositing a small quantity of a chocolate-coloured powder.

UMBER. *Umbra. Terre fine de Turquie umber. Argile ochreuse brune.*—A pigment, consisting of an argillaceous brown hæmatite, essentially $2Fe^2O^3.SiO^2.H^2O$, with alumina and manganic oxide, according to the analyses of Klaproth and v. Merz. It was originally obtained from Umbra, in the Papal States, but is now imported chiefly from Cyprus. It forms chestnut-brown to liver-brown amorphous masses, having a hardness of 1·5 to 2·5, and a specific gravity of 2·2. It feels meagre, adheres to the lips, and gives the reaction of iron. It dissolves partially in cold hydrochloric acid, and to a greater extent in hot hydrochloric acid, with evolution of chlorine. When heated it gives off water, turns dark-brown, and then constitutes the pigment called raw umber; by stronger heating, it is completely dehydrated, becoming red-brown and softer, and then constitutes burnt umber. It is used both as an oil- and water-colour, frequently mixed with other colours.

Cologne umber, Cologne-earth, or Cologne-brown is an earthy lignite, sometimes used as a pigment instead of real umber.

UNGHWARITE. A hydrated iron-silicate, allied to nontronite, occurring in Hungary, at Haar near Passau in Bavaria, and on the Meenser Steinberg, near Göttingen, in amorphous, yellowish-green to pistachio-green, opaque masses, imbedded in or mixed with opal. Its composition has not been exactly determined, inasmuch as the quantitative relations of the silica and water are rendered very variable by the admixture of opal. Von Hauer (Wien. Akad. Ber. xii. 161) obtained, as a mean of ten analyses, 57·76 per cent. silica, 20·86 ferrous oxide, 1·77 lime, and 19·78 water. Chloropal (i. 921) is merely opal coloured with unghwarite.

UNIO. The blood of *Unio pictorum* is a mobile, alkaline, slightly bluish liquid, which, after separation from the body of the mussel, deposits yellow fibrinous flocks, while the remaining liquid becomes turbid on boiling, but not when mixed with acetic or nitric acid. (Witting, J. pr. Chem. lxxiii. 121.)

UNIONITE. This name appears to have been given to two distinct minerals, viz. oligoclase and zoisite, both occurring at Unionville in Pennsylvania.

UNITARY THEORY. *Système unitaire.*—This term was applied by Gerhardt to the system of Chemistry in which the molecules of all bodies are compared, as to their magnitude, with one unit molecule—water, for example,—and all chemical reactions are, as far as possible, reduced to one typical form of reaction, namely double decomposition. This system has been fully illustrated throughout the present work, and therefore need not here be considered in further detail. (See Atomic Weights, i. 457—473; Chemical Affinity, i. 855—858; Classification, i. 1015—1022; Formulæ, ii. 695; Gases, Combination of, by Volume, ii. 809; Molecule, iii. 1027; Types, v. 926; also Gerhardt, *Introduction à l'étude de la Chimie par le système unitaire*, 1848; and further *Traité de Chimie organique*, iv. 563, *et seq.*)

UPAS is the Malay term for arrow-poison, especially for that obtained from plants (for which also, in Celebes and Borneo, the name *ipo* is used). Generally speaking, however, the term "upas" is applied to two particular arrow-poisons used in the East Indies—namely, *Upas Antjar*, and *Upas Radja*, or *Upas Tieutè*.

Upas Antjar is prepared from the milky juice of *Antiaris toxicaria*, the poison-tree of Macassar. The juice, dried at 100°, contains from 3·5 to 3·7 per cent. antiarin (i. 310), a compound which kills rabbits inoculated with $\frac{1}{30}$ grain of it, or even less. For the preparation of the arrow-poison, the juice is mixed with ground pepper, onion-juice, zerumbet, parts of a species of arum called *njampoo*, dragon's-blood, and other substances. The mixture is not boiled, but slowly inspissated to a red-brown resinous mass, which is left to dry in the sun. It resembles opium when dry, and forms a brown emulsion with water. According to Mulder, it contains, besides antiarin, a non-poisonous resin, gum, sugar, and inorganic salts. When injected into the circulation, ¼ grain of it is fatal to rabbits, ½ grain to dogs, and from 4 to 6 grains to larger animals, such as buffaloes. It likewise kills when taken into the stomach, but in that case larger doses appear to be required.

Upas Radja, or Upas Tieuté, also called Upas Tjettik, and in the remoter parts of India, Sung-sig (dagger-poison), is prepared from the younger roots, and the bark of the older roots of *Strychnos Tieuté*, a shrub growing in the forests of Java, by boiling for an hour with addition of various less essential ingredients. It is brownish-black when fresh, resembles opium when dry, has a bitter taste, is for the most part soluble in alcohol, and, according to Pelletier and Caventou, contains as its active constituents, strychnine and brucine. According to Horsfield and Mayer, it acts in the same manner as the fresh extract of *Strychnos Tieuté*. It is regarded in India as the strongest and most dangerous of arrow-poisons.

The bulbs of certain amaryllidaceous plants, *Crinum asiaticum* and *Cr. moluccanum*, which exert an emetic and diaphoretic action, are used in the East as remedies in cases of wounding by poisoned arrows.

URACONISE. Syn. with URANIUM-BLOOM.

URALITE. A pseudomorph of hornblende, after augite, from the Ural.

URALITE-PORPHYRY. An aphanite-porphyry occurring in the Ural, containing uralite, and sometimes also crystals of labradorite.

URALORTHITE. Orthite from the neighbourhood of Lake Ilmen, near Miask, in the Ural, formerly mistaken for tscheffkinite.

URAMIL. Syn. with DIALURAMIDE (ii. 315).

URAMILIC ACID. *Dialuramic Acid* (Laurent). (Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 314.—Gregory, Phil. Mag. xxiv. 187.)—Obtained by boiling a solution of dialuramide in cold sulphuric acid with water, or by evaporating a solution of thionurate of ammonium with a moderate quantity of sulphuric acid. It forms transparent four-sided prisms; or, by rapid crystallisation, silky needles; they redden litmus slightly, and turn red at about 100°, without losing weight. It dissolves in 6 or 8 pts. cold and 3 pts. hot water, and in sulphuric acid without blackening or evolution of gas. It forms crystallisable salts with the alkalis, and precipitates barium-, calcium-, and silver-salts on addition of ammonia; the silver-precipitate contains about 64 per cent. silver (Liebig and Wöhler). It dissolves quietly in cold nitric acid, but is decomposed by boiling with strong nitric acid. When it is boiled with dilute hydrochloric or sulphuric acid, dialuric acid is formed, which is partially converted into alloxantin by the action of the air. (Gregory.)

The formula assigned by Liebig and Wöhler to uramilic acid is $C^8H^{10}N^5O^{7\frac{1}{2}}$, the percentage they obtained by analysis is C, 32·09; H, 3·59; N, 23·23; O, 41·09; but they do not state at what temperature their crystals were dried. Gmelin suggests $C^8H^9N^5O^7$, which is the formula adopted by Laurent (Compt. rend. xxxv. 629), who regards the compound as dialuramic acid, $N.C^8H^6N^4O^6.H^2.H.O$. Gerhardt (*Chim. org.* i. 510), relying on Gregory's experiments, regards it as acid dialurate of ammonium, the formula of which is $C^8H^{11}N^5O^8 = C^8H^7(NH^4)N^4O^8$. F. T. C.

URANATES. Compounds of the uranic oxide with basic metallic oxides.

URANIC ACID. A name applied to uranic oxide when in combination with bases.

URANIN. Syn. with pitchblende or native oxide of uranium

URANITE. Native calcio-uranic phosphate (iv. 585).—*Chalcolite*, or *copper-uranite*, is an isomorphous mineral having the calcium replaced by copper.

URANIUM. *Atomic weight*, 120; *Symbol*, U.—Klaproth, in 1789, discovered, in pitchblende and uranite, a metallic oxide to the metal of which he gave the name uranium. Its compounds were subsequently examined by Richter, Buchholz, Lecanu, Brande, and especially by Berzelius and Arfvedson.* Péligot, in 1840, showed that the body previously regarded as metallic uranium was really the protoxide (UO); he likewise obtained the true metal, and determined its atomic weight correctly. Further examinations of uranium-compounds have been made by Ebelmen, Rammelsberg, Wertheim, Patera (J. pr. Chem. lxi. 397), Drenkmann (Jahresb. 1861, p. 255), and others.

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* For references, see *Gmelin's Handbook*, iv. 157.

Uranium is not a very abundant metal. Its principal ore is pitchblende, which consists of impure uranoso-uranic oxide; it occurs also as carbonate in liebigite (i. 798); as sulphate in johannite, or uranium-vitriol, and in uranium-ochre (p. 616); as phosphate in uranite or uranium-mica (iv. 584); as niobate and tantalate in uranotantalite or samarskite; in smaller quantity also in tyrite, bragite, fergusonite (iv. 55), pyrochlore, and polycrase (iv. 57), and as niobate and titanate in euxenite (ii. 611).

Extraction.—Uranium is almost always obtained from pitchblende, a mineral containing from 40 to 90 per cent. of uranoso-uranic oxide, U^3O^4, associated with sulphur, arsenic, lead, iron, and several other metals. The mineral is finely pounded, freed by elutriation from the finer earthy impurities; roasted for a short time to remove part of the sulphur and arsenic; then dissolved in nitric acid, and the solution evaporated to dryness. The residue is exhausted with water; the solution filtered from the brick-red residue of ferric oxide, ferric arsenate, and lead-sulphate; the greenish-yellow filtrate is slightly concentrated by evaporation, and left to cool, whereupon it deposits crystals; and the resulting radiated mass of crystallised uranic nitrate is drained on a funnel, and then washed with a small quantity of cold water. As the water dissolves a portion of the crystals, it is used in a subsequent operation to redissolve the residue obtained by evaporating the solution of pitchblende in nitric acid. The uranic nitrate, after being dried in the air, is introduced into a wide-mouthed bottle containing ether, in which it immediately dissolves; the yellow solution is left to evaporate in the air; and the resulting crystals are purified by solution in hot water and recrystallisation. The mixed mother-liquids, after dilution with water, are treated with sulphydric acid to precipitate arsenic, lead, and copper, and the filtrate is freed from oxide of iron by evaporating to dryness, and digesting the residue in water. The solution thus obtained yields a fresh crop of crystals of uranic nitrate. This salt is converted by ignition into uranoso-uranic oxide, U^3O^4, and from this the protoxide is obtained by ignition with reducing agents, and the protochloride by ignition with charcoal in a stream of chlorine-gas. (Péligot, Ann. Ch. Phys. [3], v. 5; xii. 258.)

Ebelmen digests pulverised pitchblende with hydrochloric acid, to dissolve the oxides of calcium, magnesium, manganese, and other metals; roasts the washed and dried residue with charcoal; exhausts the cooled mass with strong hydrochloric acid, to remove iron, copper, and lead as completely as possible; again roasts the washed residue, and then dissolves it in hydrochloric acid. The solution thus obtained is evaporated to dryness and again treated with water, which leaves arsenate of iron undissolved; the filtrate is treated with sulphydric acid, and evaporated to the crystallising point; and the resulting crystals of uranic nitrate are purified by recrystallisation.

Metallic uranium is obtained by decomposing the protochloride with potassium or sodium. If the mixture be heated in a platinum-crucible over a spirit-lamp, and the soluble alkaline chloride washed out by water, the uranium is obtained in the form of a black powder, or sometimes aggregated on the sides of a crucible in small plates, having a silvery lustre and a certain degree of malleability. But, by introducing into a porcelain-crucible, first a layer of sodium, then chloride of potassium, and then a mixture of chloride of potassium and protochloride of uranium (the use of the chloride of potassium being to moderate the action, which is otherwise very violent), placing the porcelain-crucible within a closed earthen crucible lined with charcoal, and heating it, first moderately, till the reduction takes place, and then strongly in a blast-furnace for fifteen or twenty minutes, the metal is obtained in fused globules. (Péligot.)

Uranium, in its compact state, is somewhat malleable and hard, but is scratched by steel. Its specific gravity is 18·4; its colour is like that of nickel or iron. When exposed to the air, it soon tarnishes, and assumes a yellowish colour. At a red heat it oxidises with vivid incandescence, and becomes covered with a bulky layer of black oxide, which protects the interior from oxidation. In the pulverulent state it takes fire at about 207°, burning with great splendour, and forming a dark-green oxide, U^3O^4. It is permanent in the air at ordinary temperatures, and does not decompose cold water. It dissolves with evolution of hydrogen in dilute acids, forming green solutions. It combines directly with chlorine, giving out great light and heat, and forming a green volatile chloride. It unites directly with sulphur at a slightly elevated temperature. (Péligot.)

Uranium forms two classes of compounds—viz., the uranous compounds, in which it is biequivalent, *e.g.* $U''O$, $U''Cl^2$, $U''SO^4$, &c.; and the **uranic compounds**, in which it is triequivalent; *e.g.*:

$\overset{\prime\prime\prime}{U}{}^2O^3$	$\overset{\prime\prime\prime}{U}{}^2\left\{\begin{matrix}O^2\\Cl^2\end{matrix}\right.$	$\overset{\prime\prime\prime}{U}{}^2\left\{\begin{matrix}O^2\\(NO^3)^2\end{matrix}\right.$	$\overset{\prime\prime\prime}{U}{}^2\left\{\begin{matrix}O^2\\(SO^4)''\end{matrix}\right.$
Oxide.	**Oxychloride.**	**Oxynitrate.**	**Oxysulphate.**

There are also two oxides of uranium, intermediate between uranous and uranic oxide. There is no chloride, bromide, iodide, or fluoride corresponding to uranic oxide, such as UCl^3; neither are there any normal uranic oxysalts analogous to the normal ferric salts, such as $\overset{\prime\prime\prime}{U}(NO^3)^3$, $\overset{\prime\prime\prime}{U}{}^2(SO^4)^3$, &c.; but all the uranic salts contain the group U^2O^2, which may be regarded as a diatomic radicle (called **uranyl** by Péligot), uniting with acid radicles in the usual proportions, and forming normal salts, thus:—

Uranic oxide, or Oxide of Uranyl	$(U^2O^2)''O$
Uranic oxychloride, or Chloride of Uranyl . . .	$(U^2O^2)''Cl^2$
Uranic nitrate, or Nitrate of Uranyl	$(U^2O^2)''(NO^3)^2$
Uranic sulphate, or Sulphate of Uranyl	$(U^2O^2)''SO^4$.

This view of the composition of the uranic compounds is, however, by no means essential, since they may also be formulated as above.

URANIUM, BROMIDES OF. *a. Uranous Bromide*, UBr^2, is obtained, in the anhydrous state, by heating a previously ignited and still warm mixture of 1 pt. uranous oxide and 6 pts. starch in a stream of bromine-vapour. It is a brown pulverulent mass, exhibiting a crystalline structure on the most strongly heated portions; it fumes in the air, and is very deliquescent. (Hermann, Jahresb. 1861, p. 260.)

By dissolving uranous hydrate in aqueous hydrobromic acid, a dark-green liquid is formed, which, when evaporated over oil of vitriol, yields dark-green crystals of hydrated uranous bromide, $UBr^2.4H^2O$; they are very deliquescent, yield an emerald-green solution, and are decomposed by heat, giving off bromine and leaving uranous oxide.

Uranic Oxybromide, $U^2O^2Br^2$, or *Bromide of Uranyl*, $(U^2O^2)''Br^2$, is produced by treating uranous oxide with bromine and water, or by dissolving uranic oxide in hydrobromic acid, and evaporating. It forms yellow needles, which have a styptic taste, give off water and become orange-yellow when heated; and at a stronger heat, in contact with the air, give off hydrobromic acid and bromine, and leave uranic oxide. They deliquesce in the air, and their solution gives, with ammonia, a precipitate of uranic hydrate. (Berthemot, Ann. Ch. Phys. [3], xliv. 387.)

URANIUM, CHLORIDES OF. Uranium forms a dichloride and an oxychloride, analogous to the bromine-compounds just described, also a subchloride analogous to the suboxide.

The *Subchloride*, U^4Cl^6, obtained by strongly igniting the dichloride in hydrogen-gas, forms a coarsely fibrous, dark-brown, slightly volatile mass. It dissolves easily in water, but the purple solution is quickly converted into uranous chloride, with evolution of hydrogen and deposition of a red powder. Ammonia throws down the hydrated suboxide.—According to Rammelsberg, a brown subchloride, U^3Cl^4, is formed by heating the dichloride in ammonia-gas.

The *Dichloride*, or *Uranous chloride*, UCl^2, is formed, with vivid incandescence, by burning metallic uranium in chlorine-gas; also by igniting uranous oxide in hydrochloric acid gas. It is prepared by passing chlorine over an intimate mixture of charcoal and either of the oxides of uranium, strongly heated in a tube of very refractory glass. It crystallises in dark-green regular octahedrons, which have a metallic lustre, and, when heated to redness, volatilise in red vapours, and form a sublimate. It is very deliquescent, fumes strongly on exposure to the air, and dissolves easily in water, with a hissing noise and great rise of temperature, forming a dark emerald-green solution, which, when evaporated in a vacuum, leaves an amorphous, green, deliquescent mass of uranous chloride; but when evaporated by heat, gives off hydrochloric acid, and leaves a residue soluble in water (probably an oxychloride). The solution of uranous chloride, when boiled, gives off hydrochloric acid and deposits a very finely-divided brown powder. When the same solution is dropped into boiling water, the whole of the uranium is precipitated as uranous hydrate. Alkalis also throw down uranous hydrate. The solution of uranous chloride is a powerful deoxidising agent, reducing gold- and silver-salts, completely converting ferric chloride into ferrous chloride, &c.

Dry uranous chloride ignited in hydrogen-gas, gives off a fourth of its chlorine, and is reduced to U^4Cl^6.—Dry ammonia-gas converts it, at ordinary temperatures, into the compound $3UCl^2.2NH^3$; at a red heat, reduction takes place, and the subchloride is produced.

Uranic Oxychloride, or *Chloride of Uranyl*, $U^2O^2Cl^2$.—When dry chlorine-gas is passed over uranous oxide at a red heat, the tube becomes filled with an orange-yellow vapour of this compound, which solidifies in a yellow crystalline mass, easily fusible, but not very volatile. When ignited with potassium, it yields chloride of potassium and uranous oxide. Dissolved in water, it forms hydrated chloride of uranyl, $U^2O^2Cl^2.H^2O$. The same solution of uranic oxychloride is formed when a solution of uranous chloride is exposed to the air, or treated with nitric acid. When evaporated, it yields, according to Klaproth, crystals which effloresce on exposure to the air; according to Arfvedson, an uncrystallisable syrup.

Uranic oxychloride forms double salts with the chlorides of the alkali-metals.—The *ammonium-salt*, $2NH^4Cl.U^2O^2Cl^2.2H^2O$, crystallises, after some time, from a syrupy solution, in very deliquescent rhombohedrons (Péligot).—The *potassium-salt*, $2KCl.U^2O^2Cl^2.2H^2O$, is obtained by dissolving uranate of potassium in excess of hydrochloric acid, adding chloride of potassium, and evaporating. The crystals dissolve readily in water; but on evaporating the resulting solution, chloride of potassium crystallises out, and uranic oxychloride remains in solution.—*Chloride of sodium* appears to form a similar double salt.—Uranic oxychloride also forms double salts with the hydrochlorates of organic bases. (C. Gr. Williams.)

URANIUM, CYANIDES OF. But little is known respecting these compounds. Uranous oxide does not dissolve in hydrocyanic acid, and the precipitate formed by cyanide of potassium in uranous solutions consists merely of hydrated uranoso-uranic oxide. (Rammelsberg.)

With uranic salts, cyanide of potassium forms a yellow precipitate, probably consisting of uranic oxycyanide. This precipitate dissolves when warmed in excess of potassium-cyanide, and is not reprecipitated therefrom by acids, perhaps in consequence of the formation of a uranium-compound analogous to ferricyanide of potassium. (Fresenius and Haidlen.)

URANIUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions.*—Uranic oxide and salts, fused with *phosphorus-salt* in the outer blowpipe-flame, produce a clear yellow glass, which becomes greenish on cooling. In the inner flame the glass assumes a green colour, becoming still greener when cold. Similar colours are obtained with *borax*. The oxides of uranium are not reduced to the metallic state by fusion with carbonate of soda on charcoal.

2. *Reactions in Solution.*—α. Uranous salts are formed by dissolving uranous oxide in strong hydrochloric or sulphuric acid, or the hydrate in dilute acids, also by reduction of uranic salts. They are green or greenish-white, and yield green aqueous solutions, from which *caustic alkalis* throw down a red-brown gelatinous precipitate of uranous hydrate; *alkaline carbonates* (with evolution of carbonic anhydride), green precipitates, which dissolve in excess of alkaline carbonate, especially of ammonium-carbonate, forming green solutions: the green precipitate, after washing and drying, consists of pure uranous hydrate. Uranous salts also yield a green precipitate with *phosphate of sodium*, grey-green with *oxalic acid*, light-brown with *ferrocyanide of potassium*. *Sulphide of ammonium* forms a black precipitate of uranous sulphide; the acid and neutral solutions are not precipitated by *sulphydric acid*. Uranous salts are easily oxidised to uranic salts by exposure to the air, or by treatment with nitric acid; they easily reduce *gold-* and *silver-salts*.

β. Uranic salts are yellow; they are mostly soluble in water, and in solution have a bitter taste, without any metallic aftertaste. They are reduced to uranous salts by *sulphydric acid*; also by *alcohol* or *ether* in sunshine.—*Caustic alkalis*, added to uranic solutions, throw down a yellow precipitate, consisting of a uranate of the alkali-metal, which is insoluble in excess of the reagent.—*Alkaline carbonates* produce a yellow precipitate, consisting of a carbonate of uranium and the alkali-metal, soluble in excess, especially in acid carbonate of potassium or acid carbonate of ammonium. Potash added to these solutions throws down all the uranic oxide. From the solution in carbonate of ammonium, the uranic oxide is likewise precipitated by boiling.—*Carbonate of barium* completely precipitates uranic oxide from its solutions at ordinary temperatures.—*Phosphate of sodium*, added to uranic salts not containing too much free acid, produces a white precipitate of uranic phosphate, having a slight tinge of yellow.—*Sulphide of ammonium* produces a black precipitate of uranic sulphide, which remains for a long time suspended in the liquid.—*Sulphydric acid* produces no precipitate.—*Ferrocyanide of potassium* produces a dark red-brown precipitate; *ferricyanide of potassium*, none.—Metallic *zinc* does not precipitate uranium in the metallic state from uranic solutions, but, after a long time, produces a yellow precipitate of uranic oxide.

4. *Estimation* and *Separation.*—Uranium is completely precipitated from uranic solutions by *ammonia*. The precipitate, which consists of hydrated uranic oxide containing ammonia, must be washed with water containing sal-ammoniac, as it runs through the filter when washed with pure water. It is then dried and ignited in an open crucible,

whereby it is converted into uranoso-uranic oxide, U^3O^4; but to obtain a perfectly definite result, and prevent further oxidation during cooling, it is necessary to put the cover on the crucible while the substance is still red-hot, and keep it there till the crucible is quite cold. The oxide thus obtained contains 84·90 per cent. of uranium. An accurate result is likewise obtained by igniting the sesquioxide in an atmosphere of hydrogen, whereby it is reduced to protoxide containing 88·24 per cent.of the metal.

If the uranic solution contains a considerable quantity of an earth or a fixed alkali, the precipitate formed by ammonia carries down with it a certain portion of the earth or alkali, to free it from which it must, before ignition, be redissolved in hydrochloric acid, and reprecipitated by ammonia.

From the alkali-metals, uranium, in the state of uranic salt, is separated by *ammonia*, attention being paid to the precaution just mentioned. A method of separating uranic oxide from alkalis, founded on the solubility of uranic silicofluoride in alcohol, is given by Stolba (*Zeitschr.* anal. Chem. iii. 71; Jahresb. 1864, p. 718).

From barium it is separated by *sulphuric acid*; from *strontium* and *calcium*, also by sulphuric acid with addition of alcohol.

From magnesium, manganese, cobalt, nickel, and zinc, these metals being in the state of protoxide, and the uranium in the state of sesquioxide, it is separated by precipitation with *carbonate of barium*.—From zinc, cobalt, and nickel it may also be separated by mixing the solution of the chlorides with excess of sodic acetate, and passing a rapid stream of sulphydric acid into the boiling liquid: the zinc, cobalt, and nickel are then completely precipitated, while the whole of the uranium remains dissolved. (Gibbs, Sill. Am. J. [2], xxxix. 58; Jahresb. 1865, p. 727.)

From iron it is separated by *carbonate of ammonia*, both metals being in the state of sesquioxide; the uranic oxide then dissolves, while the ferric oxide remains undissolved. Care must, however, be taken that the carbonate of ammonia be really monocarbonate, quite free from excess of carbonic acid, otherwise the iron will also be dissolved. To ensure this condition, the carbonate of ammonia must be previously boiled, and the solution of the oxides, if acid, must be neutralised with ammonia till a slight permanent precipitate begins to form: the solution should then be diluted with water. The uranic oxide is separated from the filtrate either by boiling, or by supersaturation with hydrochloric acid and precipitation by ammonia.

From aluminium, uranium is also separated by *carbonate of ammonia*, and with greater facility.

From cadmium, copper, lead, tin, and all other metals whose salts are insoluble in dilute acids (Group i. ANALYSIS, i. 217), uranium is separated by *sulphydric acid*; from *chromium*, in the same manner as iron is seperated from that metal (i. 945); and from vanadium, tungsten, molybdenum, and tellurium, by *sulphide of ammonium*, in which the sulphides of the last-named metals are soluble.

For the methods of separating uranium from niobium, tantalum, and titanium, see those metals (iv. 51; v. 664, 839).

Volumetric Estimation.—Acid manganic phosphate, added to an acid solution of ammonio-uranic acetate, forms a yellowish-white precipitate, which, when the precipitation is quite complete, changes its colour to yellowish rose-red (from formation of basic manganic phosphate). The reaction may be applied to the volumetric estimation of uranium, by dissolving 1 to 1½ grm. of the uranium-compound in dilute nitric or in nitromuriatic acid, supersaturating with ammonium-carbonate, then diluting the solution, and adding excess of acetic acid, till the liquid is made up to a litre. If phosphoric or arsenic acid is present, the uranium must first be precipitated by sulphide of ammonium. The normal solution of manganic phosphate is prepared by strongly heating syrupy phosphoric acid with finely-divided manganic oxide, till a dark-blue colour is produced, diluting to such a degree that 1 grm. of uranium shall correspond to 30 cubic centimetres, and titrating with pure uranous or uranic oxide. (Guyard, Bull. Soc. Chim. 1863, p. 89; Jahresb. 1863, p. 692.)

Belouheber (Bull. Soc. Chim. 1867, i. 494) estimates uranium volumetrically by means of potassic permanganate, the uranium-salt being previously brought to the minimum of oxidation by treatment with zinc and sulphuric acid.

5. *Atomic Weight of Uranium.*—Péligot, in 1842 (Ann. Ch. Pharm. xlii. 141), determined the proportion of chlorine contained in uranous chloride, UCl^2, by precipitation with nitrate of silver. Two experiments gave 39·1 and 37·2 per cent. chlorine, therefore 60·9 and 62·8 per cent. uranium. The latter, regarded by Péligot as the more correct, gives:

$$U = \frac{62{\cdot}8}{37{\cdot}2} \cdot 71 = 119{\cdot}9.$$

The analysis of uranic acetate, $U^2O^2(C^2H^3O^2)^2.H^2O$, made by Péligot, in 1845 (*ibid.* lx. 183) gave U = 120·0 and 120·1. Wertheim (J. pr. Chem. xxix. 209), by analysis of sodio-uranic acetate, and Ebelmen (Ann. Ch. Pharm. xlii. 286), by analysis of uranic oxalate, obtained somewhat lower numbers; but the number 120 is regarded as the true atomic weight of uranium.

URANIUM, FLUORIDES OF. *Uranous fluoride*, UF^2, is produced, together with uranic oxyfluoride, by the action of aqueous hydrofluoric acid on green uranoso-uranic oxide, and separates as a green insoluble powder, which passes through the filter. It is more easily prepared by boiling the yellow solution of uranic oxyfluoride, obtained as above, or a solution of ammoniacal uranic oxide or carbonate in hydrofluoric acid, with stannous chloride; the precipitate of uranous fluoride thus produced is easy to wash. Uranous fluoride is also formed by the action of hydrofluoric acid on uranous hydrate, and is thrown down by hydrofluoric acid from a solution of uranous chloride, as a bulky green precipitate. When heated in hydrogen-gas, it gives off hydrofluoric acid, and leaves a reddish mass, insoluble in water, scarcely attacked by strong nitric acid, and probably consisting of a subfluoride. (Bolton, Zeitschr. f. Chem. [2], ii. 353; Bull. Soc. Chim. 1866, ii. 450.)

Potassio-uranous fluoride, $KF.2UF^2$, is produced by the action of formic or oxalic acid, under the influence of light, on potassio-uranic oxyfluoride (*infra*). When oxalic acid is used, a precipitate of uranous hydrate is likewise formed, but it is easily separated from the double fluoride by solution in dilute acids. Potassio-uranous fluoride is a green powder resembling uranous fluoride, insoluble in water and in dilute acids, soluble in strong hydrochloric acid. Sulphuric acid dissolves it easily, eliminating hydrofluoric acid. When ignited in the air it melts, gives off hydrofluoric acid, and leaves uranate of potassium; ignited in a close vessel, it leaves a black residue of uranium-suboxide and fluoride of potassium. Caustic soda separates the suboxide from it. Heated in hydrogen-gas, it behaves like uranous fluoride. (Bolton.)

Sodio-uranous fluoride, $NaF.2UF^2$ (?), resembles the potassium-salt, but appears to be more soluble in water. When heated it does not melt, but decomposes like the potassium-salt, leaving a yellow residue of sodium-uranate. (Bolton.)

Uranic Oxyfluoride, or *Fluoride of Uranyl*, $U^2O^2F^2$.—The yellow solution, obtained by treating green uranoso-uranic oxide or uranic hydrate with hydrofluoric acid, leaves, on evaporation, a nearly white uncrystallisable mass, which dissolves in water and in alcohol (Berzelius; Bolton). It gives off water at 100°, and, when heated in the air, gives off fluorine and leaves uranium-oxide (Bolton). It forms double salts with alkaline fluorides.

The *ammonium-salt*, $(NH^4)F.U^2O^2F^2.xH^2O$, obtained like the potassium-salt (*infra*), forms indistinct crystals, soluble in water, slightly soluble in hydrofluoric acid, and insoluble in alcohol. When calcined it leaves suboxide of uranium. (Bolton.)

The *barium-salt*, $3BaF^2.2U^2O^2F^2.2H^2O$, is a yellow crystalline precipitate, insoluble in cold water, soluble in dilute acids.

The *potassium-salt*, $3KF.U^2O^2F^2$, separates, on adding fluoride of potassium in excess to uranic nitrate, as a lemon-yellow, dense, crystalline precipitate; it is also formed by dissolving uranate of potassium in hydrofluoric acid mixed with fluoride of potassium. It separates from solution in boiling water in anhydrous crystalline crusts, and is deposited by slow evaporation in macled crystals belonging to the quadratic system: it is anhydrous. When heated, it melts, with partial decomposition, to a red liquid, which solidifies to a yellow mass on cooling. It dissolves without decomposition in boiling water, forming a solution which does not attack glass. Fused with carbonate of sodium, it yields fluoride and uranate of sodium. Ignited in hydrogen, it leaves a residue consisting of uranium-fluoride, uranium-suboxide, and potassium-fluoride. By formic or oxalic acid, under the influence of light, it is reduced to potassio-uranous fluoride (Bolton).—The *sodium-salt*, $NaF.U^2O^2F^2.4H^2O$, is sometimes obtained, in fine efflorescent right rhomboïdal prisms, by evaporating a mixture of sodium-fluoride and uranic nitrate, or a solution of sodium-uranate in hydrofluoric acid; but on attempting to recrystallise it, fluoride of sodium crystallises out alone. By formic or oxalic acid it is reduced to sodio-uranous fluoride. (Bolton.)

URANIUM, IODIDES OF. *Uranous iodide*, UI^2, is obtained by dissolving uranous hydrate in hydriodic acid; the green solution, when evaporated in contact with the air, acquires a brown colour from separation of iodine, and yields a black crystalline mass, insoluble in water, and containing a small quantity of uranic oxyiodide. (Rammelsberg.)

URANIUM, OXIDES OF. Uranium forms four compounds with oxygen—viz., uranous oxide, UO; uranic oxide, U^2O^3; and two intermediate oxides, U^4O^5 and U^3O^4, which may be regarded as compounds of the other two.—A suboxide, U^4O^3, appears also to be precipitated, in combination with water, on adding ammonia to the aqueous solution of the subchloride, U^2Cl^3; but the brown precipitate thus produced, quickly takes up oxygen from the water, and is converted into a greenish-yellow hydrate, which, in contact with the air, oxidises further to uranous hydrate.

Uranous Oxide, UO.—This oxide, formerly mistaken for the metal, is obtained by exposing uranoso-uranic oxide, U^3O^4, mixed with charcoal-powder, bullock's blood, or oil, to the strongest heat of a blast-furnace; by heating the same oxide to redness in a current of dry hydrogen; by igniting uranic oxalate in a close vessel, or (better) in a current of hydrogen; or by igniting potassio-uranic chloride (p. 943), either alone or in hydrogen.

Uranous oxide obtained by the last-mentioned process forms, after washing, a metallically lustrous powder composed of microscopic regular octahedrons, translucent with red-brown colour on the edges (Arfvedson). That which is prepared from the oxalate is a cinnamon-brown or copper-red metallically lustrous powder, of specific gravity 10·15 (Péligot; Ebelmen); that prepared by reducing uranoso-uranic oxide with charcoal is an iron-grey powder, consisting of feebly lustrous microscopic needles (Bucholz). When a solution of ammonium-uranate in hydrochloric acid is evaporated with sal-ammoniac and common salt, the remaining mass heated in a covered crucible till the sal-ammoniac volatilises and the sodium-chloride melts, and the soluble salts washed out with water, uranous oxide remains in the form of a black crystalline powder (Wöhler). The black anhydrous oxide is also formed by boiling uranous hydrate with water.

Uranous oxide easily passes to a higher state of oxidation, the compact crystalline variety, however, less rapidly than the finely-divided oxide; that prepared from the oxalate at not too strong a heat is even pyrophoric. Uranous oxide, when heated, burns with a glimmering light, and is converted into uranoso-uranic oxide.

Uranous hydrate is precipitated from uranous salts by caustic alkalis, in bulky red-brown flocks, which retain a portion of alkali after washing with cold water, and turn black on boiling.

Uranous oxide, after ignition, is insoluble in dilute hydrochloric or sulphuric acid, but dissolves in strong sulphuric acid. The hydrate dissolves easily in acids, forming uranous salts. (For the reactions of those salts, see p. 943).

Uranoso-uranic Oxide, U^3O^4 – $UO.U^2O^3$.—This oxide forms the principal constituent of pitchblende. It is obtained artificially by igniting the metal or uranous oxide in contact with the air; by heating uranous oxide to redness in an atmosphere of aqueous vapour; and by gentle ignition of uranic oxide or uranic nitrate. It is a dark-green velvety powder, of specific gravity 7·1 to 7·3. When ignited alone it is reduced to the black oxide, U^4O^5; by ignition in hydrogen, or with sodium, charcoal, or sulphur, it is reduced to uranous oxide.

Pitchblende sometimes occurs in regular octahedrons, or combinations of the octahedron with the cube and rhombic dodecahedron, but more generally massive and botryoïdal. Hardness = 5·5. Specific gravity = 6·468—8. Lustre submetallic or greasy to dull. Colour greyish, greenish, brownish-red, or velvet-black. Streak brownish-black or olive-green, a little shining. Opaque. Fracture conchoïdal, uneven. It contains from 70 to 90 per cent. uranous oxide, together with sulphur, lead, arsenic, antimony, bismuth, iron, manganese, cobalt, magnesium, calcium, carbonic acid, phosphoric acid, silica, and sometimes traces of fluorine (Rammelsberg's *Mineralchemie*, p. 175). It occurs, accompanying various ores of lead and silver, at Johanngeorgenstadt, Marienberg, and Schneeberg in Saxony, at Joachimsthal and Przibram in Bohemia, and at Retzbanya in Hungary. It is associated with uranite at Tincroft and Tolcarn near Redruth in Cornwall, and at Adrianople in Turkey.

Uranoso-uranic oxide and ground pitchblende are used for producing a very permanent black colour under the glaze of porcelain.

Uranoso-uranic oxide is but little acted upon by dilute hydrochloric or sulphuric acid; but these acids, when concentrated, dissolve it without alteration; by nitric acid it is dissolved, and oxidised to uranic nitrate. A solution of uranoso-uranic acid in hydrochloric or sulphuric acid, diluted with water and mixed with ammonia, yields a grey-green precipitate of uranoso-uranic hydrate, which, if precipitated in the cold, dissolves easily and without alteration in dilute acids, but is decomposed by carbonate of ammonium, which dissolves out uranic oxide, leaving brown uranous hydrate. On mixing the solution of uranoso-uranic oxide in sulphuric acid with alcohol, uranous sulphate separates out, while uranic sulphate remains dissolved. The solution of uranoso-uranic oxide in hydrochloric acid is decomposed in the same manner on addition of sulphuric acid and alcohol. Hence it would appear that the solutions of uranoso-uranic oxide in acids are mixtures of uranous and uranic salts, a view which is likewise in accordance with their other reactions.

A black oxide of uranium, U^4O^5 or $2UO.U^2O^3$, is produced by subjecting uranic nitrate or uranate of ammonium to intense ignition, or by strongly igniting uranous oxide prepared by Wöhler's method in contact with the air. This oxide is regarded by Péligot and Drenkmann as a distinct compound; according to Rammelsberg and Ebelmen, on the other hand, it is only a mixture of green uranoso-uranic oxide with uranic oxide. If not too dense, it is oxidised by prolonged ignition in contact with the air. With acids it behaves in the same manner as the green oxide. The black colour produced upon porcelain in the manner above mentioned, probably consists of this oxide.

Uranic Oxide, or **Oxide of Uranyl,** $U^2O^3 = (U^2O^2)''O$.—Uranium and its lower oxides dissolve in nitric acid, with evolution of nitric oxide, and formation of uranic nitrate; and when this salt is heated in a basin till it begins to decompose, and then to 250° in a glass tube, as long as acid fumes continue to escape, pure uranic oxide remains in the form of a chamois-yellow powder. When ammonio-uranic carbonate (i. 797), or uranic hydrate, is heated for some time to 300°, uranic oxide remains as a brick-red powder, according to Ebelmen; according to Malaguti, however, the oxide prepared by heating the hydrate always retains a certain quantity of water. Uranic oxide, when heated to redness, gives off oxygen and leaves green uranoso-uranic oxide.

Uranic hydrate cannot be prepared by precipitating a uranic salt with alkalis, inasmuch as the precipitate always carries down alkali with it. Pure uranic hydrate may be obtained:—1. By heating uranic nitrate contained in a covered vessel in the sand-bath as long as nitric acid is given off; uranic hydrate then remains, mixed with basic nitrate, from which it may be freed by boiling with water (Berzelius).—2. A solution of uranic nitrate in absolute alcohol is evaporated at a moderate heat till, at a certain degree of concentration, nitrous ether, aldehyde, and other vapours are given off with violent intumescence, and a spongy yellow mass remains, which, when washed with boiling water, leaves uranic hydrate (Malaguti, Compt. rend. xvi. 851).—3. By exposing recently precipitated and still moist uranoso-uranic hydrate to the air (Ebelmen).—4. By boiling ammonio-uranic carbonate with water, and leaving the powder thereby separated (which contains about 2 per cent. ammonia) for some time under an imperfectly closed bell-jar (Drenkmann).—5. By fusing uranoso-uranic oxide with chlorate of potassium, and boiling out the fused mass with water.

The hydrate obtained by either of these processes contains, when dried in the air at ordinary temperatures, 11·65 per cent. water, agreeing with the formula $U^2O^3.2H^2O$. In a vacuum at ordinary temperatures, or at 100° in the air, it gives off half its water, leaving the monohydrate, $U^2O^3.H^2O$, which contains 6·11—6·28 per cent. water (by calculation, 5·88 per cent.) (Ebelmen; Malaguti). According to Drenkmann, the dihydrate prepared by the last two processes does not give off the half of its water till heated to 160°.

The monohydrate has a lemon-yellow colour, inclining to orange-yellow, and a specific gravity of 5·92. It is permanent in the air, and does not absorb carbonic acid. According to Ebelmen, it gives off all its water at 300°; but according to Malaguti, it still retains two-thirds of its water at 400°, and when more strongly heated, gives off oxygen as well as water. At a red heat it is reduced to uranoso-uranic oxide.

Uranic oxide and its hydrates dissolve in acids, forming the uranic salts (p. 943).

Uranates.—Uranic oxide unites with basic metallic oxides, forming salts called uranates. The uranates of the alkali-metals are obtained by precipitating a uranic salt with a caustic alkali; those of the earth-metals and heavy metals, by precipitating a mixture of a uranic salt and a salt of the other metal with ammonia, or by igniting a double carbonate or acetate of uranium and the other metal (calcio-uranic acetate, for example) in contact with the air. The uranates have, for the most part, the composition $M^2O.2U^2O^3$. They are yellow, insoluble in water, soluble in acids. Those which contained fixed bases are not decomposed at a red heat; but at a white heat, the uranic oxide is reduced to uranoso-uranic oxide, or by ignition in hydrogen to uranous oxide; the mass obtained by this last method easily takes fire in contact with the air.

Uranate of Ammonium is precipitated from uranic salts by ammonia, as a yellow powder, which is slightly soluble in pure water, quite insoluble in water containing sal-ammoniac, is not decomposed at 100°, but at higher temperatures gives off nitrogen, ammonia, and water. This salt sometimes occurs in commerce as a fine deep yellow colour, called "uranium-yellow." It is easily prepared by adding chloride or sulphate of ammonium to a boiling solution of sodium-uranate as long as ammonia and ammonium-carbonate are given off, washing the resulting precipitate, and drying it at a gentle heat (Anthon, Ding. pol. J. clvi. 211). This salt, when heated to redness, leaves pure uranoso-uranic oxide, and may therefore serve as the raw material for the preparation of other uranium-compounds.

Uranate of Barium, $BaO.2U^2O^3$, obtained by precipitation, as above described, is yellowish-red or orange-yellow, and when ignited in hydrogen, leaves an inflammable mixture of uranoso-uranic oxide and baryta.—The *calcium-salt* is obtained in a similar manner. Many natural uranium-ochres consist of this compound, and in that case do not give off any oxygen at a red heat.—The *lead-salt*, $PbO.2U^2O^3$, obtained by precipitation, or by repeatedly boiling carbonate of lead with fresh quantities of uranic acetate, is yellowish-red, becoming brown-red by moderate ignition; when heated in a pottery-furnace it becomes straw-yellow without undergoing reduction, and is then difficult to dissolve in acetic acid; when ignited in hydrogen, it leaves a pyrophoric mixture of uranous oxide and metallic lead (Wertheim).—The *magnesium-salt*, $MgO.2U^2O^3$, obtained by igniting magnesio-uranic acetate, is a yellow-brown powder.

The *potassium-salt*, $K^2O.2U^2O^3.3H^2O$ (Patera), is prepared by precipitating a uranic salt with excess of caustic potash; or by igniting potassio-uranic carbonate or acetate; or by fusing uranic oxide with excess of potassium-carbonate, and washing out with water. When prepared in the wet way, it is a light orange-yellow powder; when obtained by ignition, yellowish-red. It is partially reduced by hydrogen, yielding a mixture of uranoso-uranic oxide with a more basic uranate of potassium (Berzelius; Wertheim). Uranate of potassium may also be prepared from pitchblende in the same manner as the sodium-salt (*infra*). An orange-coloured potassium-uranate is produced by precipitating a solution of potassio-uranic carbonate in carbonate of potassium with caustic potash, and is prepared on the large scale by roasting pitchblende, with subsequent addition of crude potash and saltpetre (Wysocki, Dingl. pol. J. clv. 305).—An *acid salt*, $K^2O.6U^2O^3.6H^2O$, is produced by fusing acid uranic sulphate with chloride of potassium; and remains, on lixiviating the fused mass, as a yellow powder composed of microscopic rhombic prisms. It becomes brick-red by prolonged heating, and silver-grey at a white heat, in consequence of the conversion of the uranic into uranoso-uranic oxide. (Drenkmann.)

The *silver-salt*, obtained by precipitation, or by boiling argento-uranic acetate with water, is a red powder which decomposes when heated above 100°.

Sodium-salts.—The *normal salt*, $Na^2O.U^2O^3$, obtained like the potassium-salt, is yellow, and exhibits characters similar to those of the potassium-salt. By fusing it with sodium-chloride, and lixiviating with water, another salt is obtained, probably $Na^2O.U^2O^3$, in yellow six-sided tables, mixed with a small quantity of uranoso-uranic oxide (Drenkmann). By fusing uranic nitrate with sodium-chloride, and lixiviating the cooled mass, an *acid uranate of sodium*, $Na^2O.3U^2O^3$, is obtained in bronze-coloured nacreous laminæ, resembling mosaic gold, and made up of microscopic rhombic tables. It has a specific gravity of 6·91, is insoluble in water, is decomposed only at a white heat, afterwards appearing silver-grey by reflected, colourless by transmitted light, and containing uranoso-uranic oxide. (Drenkmann.)

The normal salt, $Na^2O.2U^2O^3$, is much used for imparting a yellowish or greenish colour to glass, and as a yellow pigment on the glazing of porcelain. The "uranium-yellow" for these purposes is prepared on the large scale by roasting 100 pts. of finely-pulverised pitchblende (containing 45 per cent. uranoso-uranic oxide) with 14 pts. lime in a reverberatory furnace; treating the resulting uranate of calcium with dilute sulphuric acid, by which the uranic oxide is almost completely dissolved; mixing the green solution with crude sodium-carbonate, by which the uranium is precipitated, together with other metals, but redissolved, tolerably free from impurities, by excess of the alkali; and treating the liquid with dilute sulphuric acid as long as effervescence ensues. The sodium-uranate is then precipitated as a hydrate, which becomes crystalline when dry, and then contains $Na^2O.2U^2O^3.6H^2O$ (Patera, J. pr. Chem. lxi. 397). Glass coloured with uranium-yellow is highly fluorescent.

An orange-coloured uranate of sodium may be prepared by precipitating a solution of pure sodio-uranic carbonate with caustic soda, pressing, drying, and pulverising the precipitate, then washing it, and drying it again. (Wysocki.)

Uranate of Zinc is obtained by precipitating a mixture of uranic acetate and zinc-acetate with baryta-water, or by precipitating uranic nitrate with metallic zinc, being then deposited on the metal as a compact yellow coating. (Wertheim.)

URANIUM, SULPHIDES OF. The only sulphur-compounds of uranium hitherto obtained in definite form, are uranous sulphide, US, and uranous oxysulphide, U^2S^2O. Uranic sulphide, U^2S^3, is not known with certainty.

Uranous Sulphide, US, is produced with incandescence when metallic uranium is heated in sulphur-vapour (Péligot); quickly also, but without incandescence, when uranous chloride is heated to redness in sulphydric acid (Hermann). As thus prepared, it is a greyish-black amorphous powder, which becomes crystalline when heated to whiteness out of contact with air. Uranous sulphide is also formed as a black precipitate on adding sulphite of ammonium to a solution of uranous chloride or nitrate (Hermann). When exposed to moist air, it gradually gives off sulphydric acid, and is converted into a basic sulphate; when heated in the air, it gives off sulphurous oxide, and is converted into uranoso-uranic oxide. It is not decomposed by hot hydrochloric acid, but dissolves easily in the concentrated acid. Chlorine decomposes it rapidly; nitric acid converts it into uranic sulphate.

When an oxide of uranium is ignited in a mixture of carbonic dioxide and carbonic disulphide, the higher oxides are reduced to uranous oxide, but the latter undergoes no further decomposition. Uranous oxide, and not the sulphide, is likewise produced when uranous sulphate is heated in hydrogen-gas; or when a mixture of uranous oxide and sodium-uranate is ignited with flowers of sulphur and sal-ammoniac; or when uranous sulphate is heated with persulphide of potassium. (Hermann.)

Uranous Oxysulphide, $U^2S^2O = 2US.UO$, is produced, according to Hermann, when uranous or uranoso-uranic oxide is heated to bright redness in vapour of carbonic disulphide.

Uranic Oxysulphide, or *Sulphide of Uranyl*, is precipitated, according to Remelé (Compt. rend. lviii. 716), by sulphide of ammonium from a solution of uranic nitrate. It dissolves partially in cold water, forming a brown solution, which deposits uranic oxide on standing.

Uranic Sulphide has not been obtained in the separate state; but when the precipitate formed by sulphide of ammonium in uranic salts is left for a day or two in the liquid, it is converted into a blood-red compound containing ammonium-sulphide; and this compound, when treated with potash-ley, yields a red pulverulent body containing, according to Patera, $K^2S.2U^2S^3 + 21(K^2O.2U^2O^3.3H^2O)$. The red ammonium-compound treated with the chlorides of sodium, barium, and strontium, yields corresponding red compounds containing those metals. When boiled with lime or magnesia, it turns black. (Patera, Ann. Ch. Pharm. lxxxvi. 254.)

URANIUM-BLOOM. Syn. with Uraconise (*infra*).

URANIUM-GREEN. *Uran-grün. Uranochalcite.*—These names are applied to certain decomposition-products of uranium-ores, occurring thereon in small spherical masses, or in fine needle-shaped crystals, and consisting, according to Lindacker, of uranoso-uranic sulphate mixed with calcic and cupric sulphates.

URANIUM-MICA. Syn. with Uranite (p. 940).

URANIUM-OCHRE. *Uranochre. Earthy Hydruranite. Uranite terreux.*—A term applied to various earthy uranium-minerals, such as ochry uranic hydrate and basic uranic sulphates, occurring, with or without calcic sulphate, at Joachimsthal; the latter are also called *Uraconise*, or *Zippeite.*

URANIUM-ORANGE. Orange-coloured uranates of potassium and sodium (p. 948).

URANIUM-VITRIOL. A basic uranic sulphate containing 4·0 per cent. SO^3, 79·0 U^2O^3, and 14·3 water, occurring in lemon-yellow, microscopic, rhombic prisms, at Joachimsthal in Bohemia.

URANIUM-YELLOW. A term applied to uranate of sodium, used as a pigment, and to uranate of ammonium (p. 948).

URANOCHALCITE. Syn. with Uranium-green.

URANOCHRE. Syn. with Uranium-ochre.

URANONIOBITE. A term applied by Hermann (J. pr. Chem. lxxvi. 326) to crystallised pitchblende from Norway, containing a small quantity of niobic acid.

URANOPHANE. A mineral consisting of hydrated uranic silicate, together with many other constituents, found in a mine near Kupferberg in Silesia. (Handw. d. Chem. ix. 43.)

URANOPHYLLITE. Syn. with Uranite (p. 940).

URANOPISSITE. Syn. with Pitchblende (p. 946).

URANOTANTALITE. Syn. with Samarskite, or Uranoniobate of Yttrium and Iron (iv. 55; v. 186).

URANYL. U^2O^2.—A diatomic radicle, which may be supposed to exist in the uranic compounds (p. 942).

URAO. Tetrasodic carbonate, or sesquicarbonate of soda, $Na^4H^2(CO^3)^3.2H^2O$, occurring at the bottom of a lake in Maracaibo, South America (i. 796).

URARI. Syn. with Curara (ii. 185).

URATES. See Uric Acid (p. 956).

URDITE. A mineral of unknown composition, occurring in the orthoclase of Notteröe in Norway. It has been supposed to be identical with monazite (cerous phosphate); but, according to Forbes and Dahll (J. pr. Chem. lxvi. 445), it crystallises in triclinic forms, whereas monazite is monoclinic.

UREA. COH^4N^2. *Urée. Harnstoff. Urenoxyd-ammoniak.*—This substance, isomeric with ammonium-cyanate and with carbamide, and forming the chief organic constituent of human urine, was first obtained, in an impure state, as *Extractum saponaceum urinæ*, by Rouelle the younger, in 1773, and afterwards prepared, in a state of greater purity, by Fourcroy and Vauquelin, in 1799. Wohler, in 1828 (Pogg. Ann. xii. 253; xv. 619), obtained it by molecular transformation of ammonium-cyanate, and it has been further examined, chiefly by Liebig and Wohler (*ibid.* xx. 372), Dumas (Ann. Ch. Phys. [2], xliv. 273), Pelouze (*ibid.* [3], vi. 65), Marchand (J. pr. Chem. xxxiv. 248; xxxv. 481), Werther (*ibid.* xxxv. 51), Heintz (*ibid.* xlii. 401), and Millon (Compt. rend. xxvi. 119).

Urea is contained in the urine of all mammiferous animals, especially in that of the flesh-eaters; in smaller quantity also in that of birds and of reptiles; and in the renal secretions of some animals of the lower orders. It is found in small quantity in the blood of man and of other animals in the state of health; sometimes also in the perspiration, in the amniotic liquid, in morbid exudations, and even in the tissues. It forms an essential constituent of the vitreous humour of the eye (about 30 per cent. of the solid substance, according to Millon), and has lately been found by Wurtz (Ann. Ch. Pharm. xcviii. 287) in the chyle and lymph of various animals. Its presence in the animal economy is due to the transformation of the tissues under the influence of oxygen absorbed in respiration; it is, in fact, the last term in the series of organic products of oxidation of the nitrogenous tissues.

Urea is produced artificially:—1. By the spontaneous transformation of ammonium-cyanate. A solution of this salt, when recently prepared, exhibits the reactions of cyanic acid; but when heated, or left to evaporate, it is converted into urea. Sulphocyanate of ammonium heated with oxide of silver is first converted into cyanate of ammonium, and then into urea.—2. From cyanamide, CN^2H^2, by assumption of 1 at. water, the change taking place on adding a drop of nitric acid to the aqueous solution.

3. It is obtained as a product of the decomposition of many organic bodies of complex constitution: *e.g.*, of creatine, guanine, uric acid, allantoin, &c.

Urea is commonly regarded as identical with carbamide, $N^2\left\{\begin{matrix}(CO)''\\ H^4\end{matrix}\right.$; and, consequently, the processes which give rise to this latter compound are generally spoken of as modes of formation of urea. Such are the reactions of gaseous ammonia on chloride of carbonyl, of aqueous ammonia on ethylic carbonate (i. 752), and the decomposition of oxamide by heating with mercuric oxide (Williamson, *Mémoires du Congrès scientif. de Venise*, 1847):

$$\underset{\text{Oxamide.}}{N^2(C^2O^2)''H^4} + HgO = \underset{\text{Carbamide.}}{N^2(CO)''H^4} + CO^2 + Hg.$$

But urea, though it exhibits most of the characters of an amide, especially in being resolved into carbonic acid and ammonia by the action of acids and alkalis, nevertheless does not appear to react like an amide under all circumstances. Thus, it has been lately shown by Wanklyn and Gamgee (Chem. Soc. J. xxi. 25), that urea, when heated with a great excess of potassium-permanganate in presence of much caustic potash, gives off the whole of its nitrogen in the form of nitrogen-gas; whereas, when ammonium-salts and amides are similarly heated, the whole of the nitrogen is oxidised to nitric acid. Hence Wanklyn and Gamgee regard urea as constituted differently from carbamide, and represent it by the formula $C\left\{\begin{matrix}(NH)''\\ NH^2\\ OH\end{matrix}\right.$, which is that of marsh-gas having 2 at. hydrogen replaced by imidogen, one by amidogen, and the fourth by hydroxyl. Carbamide may be represented on the same type as $C\left\{\begin{matrix}NH^2\\ NH^2\\ O''\end{matrix}\right.$, and cyanate of ammonium as $C\left\{\begin{matrix}N'''\\ O(NH^4)\end{matrix}\right.$.

Preparation of Urea.—1. From urine.—The urine is evaporated to dryness over the water-bath; the residue is exhausted with alcohol; the solution again evaporated; and the residue exhausted with absolute alcohol: the resulting solution yields, by evaporation, slightly coloured urea.—Or urine concentrated by evaporation, or by leaving it to freeze, is treated with nitric or oxalic acid, which throws down a precipitate of nitrate or oxalate of urea. The oxalate may be decomposed by chalk, which forms insoluble calcic oxalate, leaving the urea in solution (Berzelius). The nitrate of urea is decomposed in aqueous solution by carbonate of barium or potassium; the greater part of the resulting nitrate of barium or potassium is removed by evaporation and crystallisation; and the urea remaining in solution is purified by repeated crystallisation from alcohol.

2. From **cyanate of ammonium**.—The artificial preparation of urea from this salt yields a much better product than the preparation from urine. Cyanate of potassium is decomposed by sulphate of ammonium, and the resulting sulphate of potassium, which is very little soluble either in water or in alcohol, is separated from the urea formed by transformation of the ammonium-cyanate, which is very soluble in both liquids.

The following methods give good results:—*a.* A mixture of 28 pts. dry and pulverised ferrocyanide of potassium and 14 pts. manganese-peroxide is heated on an iron plate; the solution obtained by exhausting the mass with cold water is mixed with 20½ pts. dry sulphate of ammonium; the liquid is decanted from the precipitated sulphate of potassium; and the remaining portion of that salt is removed, as far as possible, by evaporation and cooling. The solution is then evaporated to dryness, and the urea is extracted from the residue by boiling alcohol (**Liebig**).—*β.* Cyanide of potassium, prepared by melting 8 pts. of the dehydrated ferrocyanide with 3 pts. carbonate of potassium, is converted into cyanate by adding 15 pts. minium to the melted mass. This salt is then dissolved out by water; the solution is mixed with 8 pts. sulphate of ammonium; the sulphate of potassium is removed as before; the filtered liquid is evaporated to dryness; and the residue is exhausted with boiling alcohol (**Clemm**, Ann. Ch. Pharm. lxvi. 382). The alcoholic solution of urea obtained by either of these methods frequently contains a certain portion of undecomposed ferrocyanide, which, however, may be easily removed by careful addition of ferrosoferric sulphate.—*γ.* According to **J. Williams** (Chem. Soc. J. xxi. 64), a better and more abundant product is obtained by digesting cyanate of lead, at a gentle heat, with an equivalent quantity of ammonium-sulphate, and evaporating the filtered liquid.

Properties.—From a pure aqueous solution, urea generally crystallises in long flattened prisms without terminal faces; but when the alcoholic mother-liquors, still containing a few impurities, are left to evaporate, the urea is obtained in slightly yellowish quadratic prisms, terminated by octahedral faces. Frequently the combination ∞P . P . oP is found at only one extremity of the prism. Angle ∞P : ∞P = 90°; ∞P : P = 139°; P : P = 82°; ∞P : oP = 90°. Urea has a cooling taste, like that of saltpetre. It dissolves in its own weight of cold water, in all proportions of hot water, and is also very soluble in alcohol (in 5 pts. of cold and 1 pt. of boiling alcohol), but nearly insoluble in ether. It melts at 120°, and decomposes at higher temperatures.

Decompositions.—1. Under various circumstances urea takes up water, and is resolved into carbonic anhydride and ammonia:

$$COH^4N^2 + H^2O = CO^2 + 2NH^3.$$

This decomposition takes place when urea is heated with *water* in sealed tubes to temperatures above 100°; or when it is boiled with *potash*, *lime*, or *magnesia*, or warmed with strong *sulphuric acid*, or evaporated with solution of *lead-acetate*; also under the influence of *ozone*, in presence of free alkali (**Gorup-Besanez**, Ann. Ch. Pharm. cxxv. 307); also by *electrolysis*. (**Schlagdenhauffen**, J. Pharm. [3], xliv. 100.)

2. In many cases urea gives up only half its nitrogen in the form of ammonia, the other half taking the form of cyanic or cyanuric acid:

$$COH^4N^2 = COHN + NH^3.$$

Thus a solution of urea evaporated with *nitrate of silver*, yields cyanate of silver and nitrate of ammonium (**Wöhler** and **Liebig**).—Urea heated with *phosphoric anhydride* yields phosphate of ammonium and cyanic acid, together with cyanuric acid, ammelide, &c.—Urea heated alone to 150°—170° is converted into biuret and cyanuric acid:

$$\underset{\text{Urea.}}{2COH^4N^2} = \underset{\text{Biuret.}}{C^2O^2H^5N^3} + NH^3.$$

$$\underset{\text{Urea.}}{3COH^4N^2} = \underset{\substack{\text{Cyanuric}\\\text{acid.}}}{C^3O^3H^3N^3} + 3NH^3.$$

But if the temperature be kept down to a few degrees above the melting-point, a white amorphous residue is obtained, consisting, according to **Gerhardt** (*Traité*, i. 406), of melanurenic acid (Gerhardt's ammeline):

$$\underset{\text{Urea.}}{4COH^4N^2} = \underset{\substack{\text{Melanurenic}\\\text{acid.}}}{C^3O^2H^4N^4} + CO^2 + 4NH^3.$$

Urea heated to 145°—160° with *phenol* also yields biuret, together with phenate of ammonium. (**Baeyer**, Ann. Ch. Pharm. cxxxi. 251.)

Hydrochlorate of urea heated to 145° yields chloride of ammonium and cyanuric acid. (**De Vry**, Ann. Ch. Pharm. lxi. 249.)

[illegible] the same [illegible] estimating [illegible]

[illegible] the weight of the [illegible] gives the [illegible]

[illegible] Ann. Ch. Pharm. lxxxv. [illegible] is based upon the [illegible] circumstance that the [illegible] is not decomposed, and therefore not turned yellow, by carbonate of sodium. 2 vols. urine are mixed with 1 vol. of a baryta-solution prepared with 2 vols. baryta-water saturated in the cold, and 1 vol. of a solution of barium-nitrate also saturated in the cold; the liquid is filtered from the precipitated sulphate and phosphate of barium; and a graduated solution of mercuric nitrate is added to a measured quantity of this filtered liquid (about 15 c.c.) till a sample taken out gives a yellow precipitate with carbonate of sodium. It is convenient to dilute the mercuric solution to such a degree that 1 cubic centimetre of it shall correspond to 0·01 grm. of urea.

Bunsen's method and that of Ragsky and Heintz give very exact results; those obtained by Millon's and Neubauer's methods are less satisfactory. Liebig's volumetric method is easy and quick of execution, and the results are very exact, when certain necessary corrections are made. (See URINE, p. 966.)

Compounds of Urea.

α. **With Acids.**—*Hydrochlorate of urea*, $COH^4N^2.HCl$, is produced, with evolution of heat, by the action of hydrochloric acid gas on urea. The product is a yellow oil, which solidifies to a crystalline mass on cooling. It is decomposed by water, and even by moist air, and is resolved by heat (at 145°) into sal-ammoniac and cyanuric acid (p. 952).

Nitrate, $COH^4N^2.HNO^3$.—This salt, the most characteristic of the urea-compounds, is moderately soluble in water, but only very slightly soluble in nitric acid. Hence a crystalline precipitate is obtained on adding nitric acid to moderately dilute solutions of urea, and a concentrated solution solidifies with nitric acid to a crystalline pulp. Nitrate of urea separates in these precipitations in shining laminæ, which appear under the microscope as rhombic or hexagonal plates, the acuter angle of which = 82°. By slow evaporation, or by cooling of a warm aqueous solution, it is sometimes obtained in well-defined prisms. It is more soluble in hot than in cold water, and dissolves also in alcohol. It is decomposed by heat (at about 140°), and detonates when suddenly heated.

Oxalate, $2COH^4N^2.C^2O^4H^2$.—This salt separates in thin crystalline laminæ, mostly grouped in tufts, when a solution of urea is mixed with a concentrated solution of oxalic acid. It dissolves easily in hot water, less easily in cold water, still less in alcohol: it is precipitated from its aqueous solution by excess of oxalic acid.

According to **Loschmidt** (Wien. Akad. Ber. li. [2], 7, 384), oxalate of urea crystallises in monoclinic usually tabular prisms, exhibiting the combination [∞P∞] . oP . ∞P . [∞P2] . [P∞] . +P . +2P∞ . Axes *a* : *b* : *c* = 1 : 0·56415 : 0·49062. Angle *b* : *c* = 82° 10′; [∞P∞] : ∞P = 112° 12′; oP : +2P∞ = 119° 4′; ∞P : +2P∞ = 134° 16′. The crystals cleave perfectly parallel to +2P∞ .

The crystalline forms of several other urea-salts have also been examined by **Loschmidt** (Wien. Akad. Ber. lii. [2], 238; Jahresb. 1865, p. 657).—The *fumarate*, $2COH^4N^2.C^4H^4O^4$, *acid maleate*, $COH^4N^2.C^4H^4O^4$, *neutral maleate*, $2COH^4N^2.C^4H^4O^4$, *acid malate*, $COH^4N^2.C^4H^6O^5$, and *succinate*, $2COH^4N^2.C^4H^6O^4$, crystallise in monoclinic forms; the *gallate*, $COH^4N^2.C^7H^6O^5$, in monoclinic but nearly rectangular prisms; the *parabanate*, $COH^4N^2.C^3H^2N^2O^3$, and the *tartrate*, $2COH^4N^2.C^4H^6O^6$, in rhombic forms; and the *citrate*, $2COH^4N^2.C^6H^8O^7$, in shining, six-sided, triclinic prisms.

β. **With Metallic Oxides.**—On adding moist *silver-oxide* to a solution of urea, a grey powder is deposited, made up of fine needles, and containing $2COH^4N^2.3Ag^2O$.

Mercuric nitrate added to a solution of urea mixed with potash, forms a white precipitate containing $COH^4N^2.2HgO$.—*Mercuric chloride* forms in the same solution a white precipitate, $2COH^4N^2.3HgO$, which turns yellow in boiling water. On adding mercuric oxide to a warm solution of urea, the compound $COH^4N^2.HgO$ appears to be produced.

γ. **With Salts.**—A solution saturated in the cold with equivalent quantities of urea and *sodium-chloride*, yields, on evaporation, shining, well-developed, monoclinic prisms of the compound $COH^4N^2.NaCl.H^2O$.—A boiling very concentrated aqueous solution of 1 at. *sodium-nitrate* mixed with 1 at. urea, deposits, on cooling, long prismatic crystals of the compound $COH^4N^2.NaNO^3.H^2O$. Urea likewise forms crystallisable compounds with the nitrates of potassium, calcium, and magnesium, chloride of cadmium, and mercuric chloride.

With *nitrate of silver*, urea forms the two compounds, $COH^4N^2.AgNO^3$ and $COH^4N^2.2AgNO^3$. The former is obtained in large rhombic prisms, when solutions of urea and silver-nitrate are mixed together, either cold or warm. The second separates in prismatic crystals, by evaporation in a vacuum, from a solution containing an excess of the silver-salt.

δ. **With Nitric Anhydride and Mercuric Oxide.**—Mercuric nitrate added to a solution of urea forms a white precipitate, the composition of which varies according to circumstances. When the two solutions are dilute, and mixed while warm, the flocculent precipitate formed at first quickly changes to a white granular powder containing $2COH^4N^2.N^2O^5.4HgO$. When a solution of silver-nitrate is poured into a solution of urea as long as a precipitate is formed, and this precipitate is exposed for some time to a temperature of 40°—50°, it is transformed into a mass of six-sided shining laminæ, consisting of $2COH^4N^2.N^2O^5.3HgO$. Lastly, when a solution of nitrate of urea is mixed with an acid solution of mercuric nitrate till turbidity ensues, the liquid deposits, on standing, crystalline crusts made up of small tabular crystals of the compound $COH^4N^2.N^2O^5.2HgO$. (Liebig.)

The composition of these three compounds is not yet definitely fixed; it is not known, indeed, whether they contain mercuric oxide and nitrate of urea, or urea combined with mercuric nitrate and mercuric oxide.

Substitution-derivatives of Urea.—Compound Ureas.

These bodies have already been described as carbamides (i. 753). They must, however, be regarded as derivatives of urea, not of carbamide, if carbamide and urea are really distinct compounds; for those which contain acid radicles are produced by the action of acid chlorides upon urea itself; and those containing alcohol-radicles are obtained by processes exactly analogous to those which yield normal urea—viz., by the action of ammonia on cyanic ethers, or of amine-bases on cyanic acid or cyanic ethers. Corresponding derivatives of carbamide might be produced by the action of amines on phosgene or on carbonic ethers, but the reaction does not appear to have been tried.

Ureas containing two atoms of alcohol-radicle are likewise formed by the action of water on cyanic ethers, an amine being produced in the first instance, and then combining with the rest of the cyanic ether; thus:

$$\underset{\substack{\text{Ethylic}\\\text{cyanate.}}}{CO(C^2H^5)N} + H^2O = CO^2 + \underset{\text{Ethylamine.}}{(C^2H^5)H^2N}.$$

$$\underset{\substack{\text{Ethylic}\\\text{cyanate.}}}{CO(C^2H^5)N} + (C^2H^5)H^2N = \underset{\text{Diethylurea.}}{COH^2(C^2H^5)^2N^2}.$$

Diethylurea is also produced by distilling the oily body, $C^8H^{17}N^3O^3$, formed by the action of potash on cyanuric ether (ii. 293):

$$C^8H^{17}N^3O^3 = \underset{\substack{\text{Ethylic}\\\text{cyanate.}}}{CO(C^2H^5)N} + \underset{\text{Diethylurea.}}{COH^2(C^2H^5)^2N^2}.$$

Polymeric ureas containing ethylene are produced by the action of cyanic acid or the cyanic ethers on ethylene-diamines (ii. 595):

$$\underset{\substack{\text{Chloride of ethy-}\\\text{lene-diammonium.}}}{(C^2H^4)''H^6N^2Cl^2} + \underset{\substack{\text{Cyanate of}\\\text{silver.}}}{2COAgN} = 2AgCl + \underset{\text{Ethylene-urea.}}{C^2O^2H^6(C^2H^4)''N^4}.$$

The properties and reactions of the compound ureas are analogous to those of urea itself. They mostly crystallise in deliquescent prisms, easily soluble in water and in alcohol. They form crystallisable compounds with nitric acid, but on the whole do not unite with acids so easily as normal urea. Those which contain only 1 at. alcohol-radicle are resolved by heat into cyanic acid and an amine-base. Dimethylurea and diethylurea are volatile without decomposition; or, rather, they are reproduced, during the distillation, by the combination of the products (cyanuric ether and ethylamine, for example) resulting from their decomposition in the earlier stage of the process.

UREIDES. Compounds containing the elements of a urea-salt minus water. (See URIC ACID, p. 958.)

URET. This name has been applied to the group CH^2NO, which, by substitution for 1 at. hydrogen in ammonia, may be supposed to form urea, $\left.\begin{matrix}CH^2NO\\H^2\end{matrix}\right\}N$, and by substitution for 2 at. hydrogen, biuret, $\left.\begin{matrix}(CH^2NO)^2\\H\end{matrix}\right\}N$ (i. 600).

URETHAMYLANE. Syn. with AMYLIC CARBAMATE.

URETHANE. A name first applied to ethylic carbamate, afterwards extended to all carbamic ethers (i. 750).

URETHYLANE. Syn. with METHYLIC CARBAMATE.

URIC ACID. $C^5N^4H^4O^3$. *Lithic acid. Harnsäure.*—This important acid was discovered by Scheele in 1776, but was first submitted to a minute examination by

Liebig and Wöhler in 1838 (Ann. Ch. Pharm. xxvi. 241). Its reactions and transformations have also been examined by Brugnatelli (Ann. Ch. Phys. [2], viii. 201), who discovered alloxan; by Prout (Ann. Phil. xiv. 363), who discovered murexide; further by Gregory (Ann. Ch. Pharm. xxxiii. 334; lx. 267), Schlieper (*ibid.* lv. 252; lvi. 1; lxvii. 231), Pelouze (Ann. Ch. Phys. [3], vi. 71), and, more especially of late years, by Baeyer (Ann. Ch. Pharm. cxxvii. 199; cxxx. 129; cxxxv. 312; Jahresb. 1863, p. 621; 1864, p. 632; 1865, p. 362), who has discovered a considerable number of new derivatives of uric acid, and given the most complete and connected account of the uric acid group of compounds yet published.

Uric acid is a product of the incomplete oxidation of animal tissue. In combination chiefly with ammonia, it forms the principal urinary constituent voided by insects, land-reptiles, and birds (whence it is found in guano). Normally it occurs, but in small proportion, in the urine of man, and is found in yet smaller proportions in that of carnivorous quadrupeds, and can scarcely be said to exist in that of herbivorous and omnivorous quadrupeds.

According to various authorities, it is constantly present in the juices of the human spleen, liver, lungs, and brain. The merest traces of it are also met with normally in blood; but in certain forms of disease, such as albuminaria, and more especially gout, its proportion in the blood becomes very appreciable. In certain cases of gout, indeed, all the fluids of the body are found more or less saturated with uric acid, and some of them even supersaturated, so as to deposit the concretions of sodium-urate, commonly known as chalk-stones. Lastly, the excess of it, occurring under greater or less derangement of bodily health, is frequently discharged by the kidneys, and deposited in the form of urinary sediment, gravel, or calculus.

No artificial method of producing uric acid has yet been discovered.

Preparation.—The best material for preparing uric acid is the excrement of serpents. This substance, which consists chiefly of ammonium-urate, is boiled with dilute potash or soda-ley, till completely dissolved; and the filtered solution is supersaturated with hydrochloric or dilute sulphuric acid, whereby the uric acid is thrown down as a flocculent gelatinous precipitate, which soon becomes crystalline. Potash is better adapted for the purpose than soda, because urate of potassium is much more soluble than urate of sodium.

Uric acid may also be prepared from guano, by boiling that substance with a dilute solution of borax (1 pt. borax to 120 pts. water), whereby a solution of sodium-urate is obtained, and precipitating with hydrochloric acid.

Properties.—Uric acid precipitated by hydrochloric acid is anhydrous, and forms small perfectly white crystalline scales. When slowly deposited from dilute solutions, it sometimes separates in large crystals containing $C^5H^4N^4O^3.2H^2O$. It is nearly insoluble in *water*, 1 pt. of it requiring 15,000 pts. of cold and 1,800 pts. of boiling water to dissolve it; in *alcohol* and *ether* it is quite insoluble. Concentrated *sulphuric acid* dissolves it abundantly when heated, and the solution, on cooling, deposits a very deliquescent compound, containing $C^5N^4H^4O^3.4SO^4H^2$, according to Fritzsche; $C^5N^4H^4O^3.2SO^4H^2$, according to Lowe (Bull. Soc. Chim. 1867, i. 442). Water added to the solution precipitates the uric acid.

Decompositions.—1. Dry uric acid, when heated, decomposes without melting, giving off hydrocyanic acid, yielding a sublimate of cyanuric acid, cyanate of ammonium, urea, and carbonate of ammonium, and leaving a carbonaceous residue.—Uric acid heated with *water* for some time to 180°, undergoes a decomposition, the chief product of which is mycomelic acid (Hlasiwetz, Ann. Ch. Pharm. ciii. 211):

$$C^5N^4H^4O^3 = C^4N^4H^4O^2 + CO.$$

An alkaline solution of uric acid boiled for a considerable time yields uroxanic acid, together with formic acid, oxalic acid, and urea.—3. Uric acid fused with *hydrate of potassium*, gives off ammonia, and leaves a residue containing oxalate, carbonate, and cyanate of potassium.

4. Dry uric acid is not attacked by dry *chlorine* at ordinary temperatures, but when heated in the gas, it is decomposed, yielding cyanic acid together with other products. When chlorine acts upon uric acid in presence of water, alloxan and parabanic acid are produced in the first instance, and ultimately carbonic acid, oxalic acid, and ammonia. According to L. Hardy (Ann. Ch. Phys. [4], ii. 372), uric acid suspended in water is converted by *bromine*, at ordinary temperatures, into alloxan and urea:

$$C^5N^4H^4O^3 + Br^2 + 2H^2O = C^4N^2H^2O^4 + CN^2H^4O + 2HBr.$$

If the mixture becomes heated during the reaction, parabanic acid, oxalic acid, and bromide of ammonium are likewise produced. *Chlorine* and *iodine* act in like manner.

Most *oxidising substances* convert uric acid into alloxan or parabanic acid; when boiled with *water* and *peroxide of lead*, it yields allantoin.—With *chlorous acid*, it yields, according to **Schiel** (Ann. Ch. Pharm. cxli. 78), a chlorinated acid called **chloraluric acid** (i. 884).—*Ozone* is quickly absorbed by uric acid, forming allantoin and urea, together with other products (**Gorup-Besanez**, *ibid.* cx. 433). Uric acid boiled with a solution of *potassium-ferricyanide* containing caustic potash, yields carbonate of potassium and allantoin, part of which is ultimately converted into lantanuric acid and urea.

Detection and Estimation.—Uric acid may be recognised by its insolubility in water and in hydrochloric acid, and by its crystalline character under the microscope (generally rhombic tables with the obtuse angles rounded off, and often associated with dumbbell-shaped crystals*), and especially by its reaction with *nitric acid.* On moistening it with nitric acid, and evaporating at a gentle heat, a yellow or reddish residue is obtained, which assumes a fine violet-red colour when treated with ammonia, and violet-blue with potash (murexide and purpurate of potassium, iv. 748). Another very delicate reaction is given by **Schiff** (Ann. Ch. Pharm. cix. 65). The uric acid is dissolved in *carbonate of sodium*, and a drop of the solution is laid on paper moistened with *silver-solution;* if uric acid is present, a brown spot is formed, carbonate of silver being reduced by uric acid at ordinary temperatures.

For the quantitative estimation of uric acid in urine, the liquid is mixed with hydrochloric acid, and left to stand for twenty-four hours, and the pulverulent deposit of uric acid is weighed. (See URINE, p. 967).

Urates.—Uric acid is dibasic. Its salts are but sparingly soluble in water, much more easily in alkaline liquids, especially when heated, freely soluble also in solutions of borax. They have been examined chiefly by **Bensch** (Ann. Ch. Pharm. liv. 189; lxv. 181).

Acid urate of ammonium, $C^5N^4H^3(NH^4)O^3$, is produced whenever uric acid and ammonia come in contact, and usually forms a white amorphous mass, but is deposited in fine needles from a solution containing excess of ammonia. It dissolves in 1,800 pts. of cold water. This salt occurs, together with free uric acid, in the excrements of birds and serpents. The neutral ammonium-salt is not known.

Potassium-salts.—The *neutral salt*, $C^5N^4H^2K^2O^3$, is obtained by saturating a cold dilute solution of potash, free from carbonate, with uric acid, and boiling down the solution in a retort. At a certain degree of concentration, the salt is deposited in fine anhydrous needles, which may be purified by decanting the clear liquid and washing with dilute alcohol. It dissolves in 44 pts of cold and 35 pts. of boiling water; the solution is slowly decomposed by boiling. The salt has a caustic taste, and quickly absorbs carbonic acid from the air.—The *acid salt*, $C^5N^4H^3KO^3$, is precipitated in a granular form on passing carbonic acid gas through a solution of the neutral salt. It dissolves in 800 pts. of cold and in about 80 pts. of boiling water, from which solution it is deposited, on cooling, in amorphous flocks.

There are two *urates of sodium*—the *neutral salt*, containing $C^5N^4H^2Na^2O^3.H^2O$ and the *acid salt*, $C^5N^4H^3NaO^3$. Both are less soluble than the corresponding potassium-salts.

Urate of Lithium is more soluble than any of the other alkaline urates: hence lithia-water is sometimes proscribed to gouty patients, and others who suffer from a superabundance of that acid.

Urates of Barium.—The *neutral salt*, $C^5N^4H^2Ba''O^3$, is obtained by adding uric acid to a boiling saturated solution of baryta, keeping the latter in excess. One pt. of it dissolves in 7,900 pts. of cold and 1,790 pts. of boiling water.—The *acid salt*, $C^{10}N^8H^6Ba''O^6$, produced by boiling uric acid with water and carbonate of barium, is a white powder, insoluble in water and in alcohol.

Urates of Strontium.—These salts are prepared like the barium-salts.—The *neutral salt*, $C^5N^4H^2Sr''O^3.2H^2O$, appears under the microscope as a mass of fine needles grouped in stars. It absorbs moisture from the air; gives off its water of crystallisation at 165°; decomposes at 170°; dissolves in 4,300 pts. of cold and 1,790 pts. of boiling water.—The *acid salt*, $C^{10}N^8H^6Sr''O^6.2H^2O$, is white, amorphous, insoluble in alcohol and in ether. One pt. of it dissolves in 603 pts. of cold and 276 pts. of boiling water.

Urates of Calcium.—The *neutral salt*, $C^5N^4H^2Ca''O^3$, is obtained by dropping a solution of the neutral potassium-salt into a boiling solution of calcium-chloride till a permanent precipitate begins to form, and boiling the solution for an hour; urate of calcium is then deposited in anhydrous grains, soluble in 1,500 pts. of cold and 1,440 pts. of boiling water.—The *acid salt*, $C^{10}N^8H^6Ca''O^6.2H^2O$, separates, on mixing chloride of calcium with a boiling solution of acid urate of potassium, as an amorphous precipitate, soluble in 603 pts. of cold and 276 pts. of boiling water, much more soluble in water containing chloride of potassium.

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* These crystals have been supposed to consist of ammonium-oxalurate, but their nature has not been exactly ascertained.

Urate of Magnesium.—The neutral salt is not known.—The *acid salt*, $C^{10}N^8H^6Mg''O^6.6H^2O$, separates, after two or three hours, from a mixture of magnesium-sulphate and acid potassium-urate, in silky nodules, which often float at the surface of the liquid. The solution of these nodules in boiling water deposits needles, which at 170° give off 19·2 per cent. water of crystallisation, corresponding to rather less than 5 at. H^2O.

Urates of Copper.—The *cupric salt* is a green precipitate, which turns brown when boiled with water. A solution of uric acid in potash produces, in an alkaline cupric solution, a white crystalline precipitate of *cuprous urate*, which is permanent in the air, is decomposed by hydrochloric acid, yielding uric acid and cuprous chloride, does not undergo any alteration in hot water or potash-ley, but when boiled with the alkaline cupric solution, is converted into red cuprous oxide (Berlin, J. pr. Chem. lxxxi. 184). Babo and Meissner (Jahresb. 1858, p. 639) have applied this reaction to the volumetric estimation of uric acid; but the results do not appear to be very trustworthy.

Urate of Lead, $C^{10}N^8H^6Pb''O^6$, is obtained—by dropping a dilute solution of neutral potassium-urate into a boiling dilute solution of lead-nitrate, separating the yellow precipitate which first forms, and adding a fresh portion of the potassium-salt to the filtrate—as a white amorphous precipitate, apparently anhydrous, and quite insoluble in water and in alcohol.

Urate of Silver is a white amorphous precipitate, which quickly suffers reduction.

ETHYLURIC ACIDS. (Drygin, Jahresb. 1864, p. 630.)—Neutral urate of lead heated with excess of ethylic iodide to 100° for 24 hours, or to 120° for 12 hours, yields—together with iodide of lead—two ethylic derivatives of uric acid: namely, diethyluric acid, $C^5N^4H^2(C^2H^5)^2O^3$, and triethyluric acid, $C^5N^4H(C^2H^5)^3O^3$, which may be separated by cold ether-alcohol, the latter only dissolving therein.

Diethyluric acid, the most abundant product of the reaction, dissolves in water and in alcohol, but not in ether, remains as an amorphous mass when its alcoholic solution is evaporated, and crystallises from hot water in broom-shaped groups of short obtuse needles, which sublime with difficulty. It dissolves in cold potash-ley, and is precipitated therefrom by hydrochloric acid, in amorphous flocks which turn red after some time. It is decomposed by heating with dilute hydrochloric acid, but the products have not been examined. Iodide of ethyl converts it into the triethylated compound.

Triethyluric acid is soluble in ether, alcohol, and hot water, crystallises in small slender needles, melts when carefully heated, and sublimes very easily. It dissolves in potash, and is precipitated therefrom by hydrochloric acid in white needles. When heated with hydrochloric acid it gives off gas, and yields a product having the composition, but not the properties, of diethyluric acid.

Products formed from Uric Acid by Oxidation, &c.

Uric acid is remarkable for the facility with which it is altered by oxidising agents, and the great number of definite and crystallisable compounds obtained in this manner, or by treating the immediate products of oxidation with acids, alkalis, reducing agents, &c. The following is a list of the principal compounds thus produced:—

Uric acid . .	$C^5N^4H^2O^3.H^2$	Thionuric acid .	$C^4N^3H^3O^6S.H^2$
Pseudo-uric acid	$C^5N^4H^5O^4.H$	Hydurilic acid .	$C^4N^4H^4O^6.H^2$
Uroxanic acid .	$C^5N^4H^8O^6.H^2$	Allantoin . .	$C^4N^4H^6O^3$
Alloxan . .	$C^4N^2H^2O^4$	Glycoluril . .	$C^4N^4H^6O^2$
Alloxanic acid .	$C^4N^2H^2O^5.H^2$	Mycomelic acid .	$C^4N^4H^3O^2.H$
Alloxantin .	$C^8N^4H^4O^7.3H^2O$	Oxaluric acid .	$C^3N^2H^3O^4.H$
Barbituric acid .	$C^4N^2H^2O^3.H^2$	Allanturic acid .	$C^3N^2H^3O^3.H$
Bromobarbituric acid	$C^4N^2H^2BrO^3.H$	Hydantoin . .	$C^3N^2H^4O^2$
Dibromobarbituric acid	$C^4N^2H^2Br^2O^3$	Hydantoic acid .	$C^3N^2H^5O^3.H$
		Allituric acid .	$C^6N^4H^5O^4.H$
Violuric acid .	$C^4N^3H^2O^4.H$	Leucoturic acid .	$C^6N^4H^3O^5.H$
Dilituric acid .	$C^4N^3H^2O^5.H$	Parabanic acid .	$C^3N^2H^2O^3$
Violantin . .	$C^4N^6H^6O^9$	Dibarbituric acid .	$C^8N^4H^4O^5.H^2$
Dialuric acid .	$C^4N^2H^3O^4.H$	Murexide . .	$C^8N^6H^8O^6$
Uramil . .	$C^4N^3H^5O^3$	Mesoxalic acid .	$C^3O^5H^2$

When uric acid is subjected to an oxidising agent, in presence of water, it gives up two of its hydrogen-atoms to the oxidising agent, while the dehydrogenised residue (which may be called **dehyduric acid**) reacts with water to form **mesoxalic acid** and **urea**:

$$C^5N^4H^2O^3 + 4H^2O = \underset{\text{Mesoxalic acid.}}{C^3H^2O^5} + \underset{\text{Urea.}}{2CN^2H^4O.}$$

Dehyduric acid.

The separation of the urea generally takes place, however, by two stages, the first portion being removed more easily than the second; thus, when dilute nitric acid acts upon uric acid, alloxan is produced; and this, when heated with baryta-water, is further resolved into mesoxalic acid and urea:

$$\underset{\text{Dehyduric acid.}}{C^5N^4H^2O^3} + 2H^2O = \underset{\text{Alloxan.}}{C^4N^2H^2O^4} + \underset{\text{Urea.}}{CN^2H^4O.}$$

$$\underset{\text{Alloxan.}}{C^4N^2H^2O^4} + 2H^2O = \underset{\text{Mesoxalic acid.}}{C^3H^2O^5} + \underset{\text{Urea.}}{CN^2H^4O.}$$

Moreover, the urea is frequently resolved into carbonic acid and ammonia by the action of the acids or alkalis present.

Alloxan is a monureide of mesoxalic acid—that is to say, it is a compound of that acid with one atom of urea minus $2H^2O$; and the hypothetical dehyduric acid is the diureide of the same acid, derived from it by addition of 1 at. urea and subtraction of 4 at. water. Now, by hydrogenising mesoxalic acid, we obtain **tartronic acid**, $C^3H^4O^5$; and by hydrogenising alloxan, we obtain **dialuric acid**, which two bodies, accordingly, bear to uric acid the same relation that mesoxalic acid and urea bear to dehyduric acid: thus—

$C^3H^2O^5.$	$C^4N^2H^2O^4.$	$C^5N^4H^2O^3.$
Mesoxalic acid.	Alloxan.	Dehyduric acid.
$C^3H^4O^5.$	$C^4N^2H^4O^4.$	$C^5N^4H^4O^3.$
Tartronic acid.	Dialuric acid.	Uric acid.

And just as the hypothetical dehyduric acid yields mesoxalic acid and alloxan, so should actual uric acid yield tartronic and dialuric acids. These bodies, however, have not been obtained by the direct breaking-up of uric acid, but only by rehydrogenising the mesoxalic acid and alloxan which result from the breaking-up of its dehydrogenised product.

Provisionally, however, dialuric and uric acids may be regarded as tartron-ureide and tartron-diureide, respectively.

The several bodies just mentioned are typical of three well-defined classes of compounds, to one or other of which an immense number of uric acid products may be referred. First, there is the class of simple non-nitrogenous acids, or **an-ureides**, like tartronic and mesoxalic acid; secondly, there is a class of bodies containing a residue of the acid plus one residue of urea—these are the **mon-ureides**, such as dialuric acid and alloxan; and, lastly, the class of bodies containing a residue of the acid plus two residues of urea, or the **di-ureides**, such as uric acid itself.

Mesoxalic acid, the most complex non-nitrogenous product obtainable directly from uric acid, constitutes the third term in the following series:

An-ureides.

CH^2O^3, Carbonic acid,
$C^2H^2O^4$, Oxalic acid,
$C^3H^2O^5$, Mesoxalic acid,

each of which contains 1 at. carbonic oxide, CO, more than the preceding. Now, when mesoxalic acid is acted upon by nascent oxygen, its excess of carbonic oxide is removed in the form of carbonic dioxide, and it is thus converted into oxalic acid:

$$\underset{\text{Mesoxalic acid.}}{C^3H^2O^5} + O = CO^2 + \underset{\text{Oxalic acid.}}{C^2H^2O^4.}$$

Hence, when uric acid is subjected to a more active oxidation than that which suffices to produce mesoxalic acid, we obtain oxalic acid, which may occur either in its simple anureide state, or conjugated with 1 at. urea to form a monureide, such as **parabanic acid**; or with 2 at. urea to form a diureide, such as **mycomelic acid**, a body related to oxalic acid just as uric acid is related to mesoxalic acid.

In like manner, when uric acid is subjected to a still more powerful oxidation than suffices to produce oxalic acid, we obtain carbonic acid, which, like oxalic and mesoxalic acids, is also capable of giving rise to ureides. No ureide of carbonic acid has, indeed, yet been formed directly from uric acid, the active treatment required to effect the complete oxidation of the uric acid producing also a separation from one another of the resulting carbonic acid and urea, which, however, may be obtained in combination by other means. Allophanic acid, for instance, is a monureide of carbonic acid; but no diureide of this acid appears to have been yet produced.

Alloxan, the monureide of mesoxalic acid above mentioned, is formed from mesoxalate of urea by elimination of 2 at. water; but there is another monureide, namely alloxanic acid, which differs from the original salt by only 1 at. water. Similarly, oxalic acid forms two monureides—namely, parabanic acid or paraban, analogous to alloxan; and oxaluric acid, analogous to alloxanic acid. Carbonic acid, however, forms but a single ureide, which is produced by the elimination of only 1 at. water, and accordingly belongs to the same series as the oxaluric and alloxanic acids: thus—

Acids.	*Ureides.*
CH^2O^3, Carbonic.	$C^2N^2H^4O^3$, Allophanic acid.
$C^2H^2O^4$, Oxalic.	$C^3N^2H^4O^4$, Oxaluric acid. $C^3N^2H^2O^3$, Paraban.
$C^3H^2O^5$, Mesoxalic.	$C^4N^2H^4O^5$, Alloxanic acid. $C^4N^2H^2O^4$, Alloxan.

Similarly, among the diureides, some are formed from the corresponding monureides by elimination of one atom, and others by elimination of two atoms of water.

Mesoxalic acid, as already observed, is convertible, by deoxidation or hydrogenation, into tartronic acid, and by pushing the deoxidation a stage further, malonic acid is obtained, both of which acids are capable of forming monureides and diureides; and, in a similar manner, oxalic and carbonic acids furnish a variety of similar deoxidation-products.

Of the numerous compounds belonging to the uric acid group thus produced, the most important are included in the following table,* which is divided perpendicularly into three columns of an-ureides, mon-ureides, and di-ureides, and horizontally into three layers of carbonic, oxalic, and mesoxalic products. The compounds connected by dotted lines differ in composition from one another by an excess or deficit of one atom of urea minus one atom of water, while those standing on the same level in the adjoining columns, and unconnected by dotted lines, differ from one another by an excess or deficit of one atom of urea minus two atoms of water:—

An-ureides.	*Mon-ureides.*	*Di-ureides.*
CH^2O^3, Carbonic.	$C^2N^2H^4O^3$, Allophanic.	
	$C^3N^2H^6O^2$, Aceturea.	
	$C^3N^2H^6O^3$, Glycoluric.	$C^4N^4H^6O^2$, Glycoluril.
		$C^4N^4H^6O^3$, Allantoin.
$C^2H^4O^2$, Acetic.		
$C^2H^4O^3$, Glycollic.	$C^3N^2H^4O^2$, Hydantoin.	
$C^2H^4O^4$, Glyoxylic.	$C^3N^2H^4O^3$, Lantanuric.	$C^4N^4H^4O^2$, Mycomelic.
	$C^3N^2H^4O^4$, Oxaluric.	
$C^2H^2O^3$, Glyoxalic.		
$C^2H^2O^4$, Oxalic.	$C^3N^2H^2O^3$, Parabanic.	
		$C^5N^4H^4O$, Hypoxanthine.
$C^3H^4O^4$, Malonic.	$C^4N^2H^4O^3$, Barbituric.	$C^5N^4H^4O^2$, Xanthine.
$C^3H^4O^5$, Tartronic.	$C^4N^2H^4O^4$, Dialuric.	$C^5N^4H^4O^3$, Uric acid.
	$C^4N^2H^4O^5$, Alloxanic.	$C^5N^4H^6O^4$, Pseudo-uric.
$C^3H^2O^5$, Mesoxalic.	$C^4N^2H^2O^4$, Alloxan.	

Between some of the consecutive monureides shown in this table, there exist bodies formed by the union of the two consecutive monureides, with elimination of water. Such is the mode of formation of alliturie, lantanuric, and hydurilic acids, and of alloxantin; thus:

$$\underset{\text{Alliturie acid.}}{C^6N^4H^6O^4} = \underset{\text{Hydantoin.}}{C^3N^2H^4O^2} + \underset{\text{Lantanuric acid.}}{C^3N^2H^4O^3} - H^2O.$$

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* Odling's "Lectures on Animal Chemistry" (London, 1866) p. 133.

$$\underset{\text{Leucoturic acid.}}{C^6N^4H^4O^5} = \underset{\text{Lantanuric acid.}}{C^3N^2H^4O^3} + \underset{\text{Parabanic acid.}}{C^3N^2H^2O^3} - H^2O.$$

$$\underset{\text{Hydurilic acid.}}{C^8N^4H^6O^6} = \underset{\text{Barbituric acid.}}{C^4N^2H^4O^3} + \underset{\text{Dialuric acid.}}{C^4N^2H^4O^4} - H^2O.$$

$$\underset{\text{Alloxantin.}}{C^8N^4H^4O^7} = \underset{\text{Dialuric acid.}}{C^4N^2H^4O^4} + \underset{\text{Alloxan.}}{C^4N^2H^2O^4} - H^2O.$$

All the compounds above formulated are described in their alphabetical places, except barbituric acid, glycoluril, glycoluric acid, and some derivatives of acetylurea or aceturcide.

1. *Oxalic Monureides.*—Glycoluric acid, $C^3N^2H^6O^3$, appears to be identical with Baeyer's hydantoic acid (iii. 177).

The barium-salt of this acid is produced, together with urea, by heating glycoluril (p. 961) with baryta-water:

$$\underset{\text{Glycoluril.}}{C^4N^4H^6O^2} + 2H^2O = \underset{\text{Glycoluric acid.}}{C^3N^2H^6O^3} + \underset{\text{Urea.}}{CN^2H^4O}.$$

The urea, however, splits up, in presence of the baryta, into carbonic acid and ammonia, so that carbonate of barium is deposited and ammonia given off.

The glycolurate of barium remains in solution, and by decomposing this solution with dilute sulphuric acid and evaporating the filtrate, glycoluric acid is obtained in transparent crystals. Its dilute solution, treated with silver-oxide in excess, yields an alkaline liquid, which gradually deposits a silver-salt, $C^3N^2H^5AgO^3$, in fine pearly scales and warty tufts of white needles; on acidulating with nitric acid, or adding nitrate of silver, the pearly scales are deposited immediately. (Rheineck, Ann. Ch. Pharm. cxxxiv. 219.)

Lantanuric acid, $C^3N^2H^4O^3$, is probably identical with the allanturic acid of Pelouze (i. 132), and with diffluan (ii. 322).

The relations of lantanuric and oxaluric acid to one another, and to another uric acid product called oxaluramide (iv. 277), are the same as those of hydrogen and water to ammonia:

H.H, hydrogen. . . . . $C^3N^2H^3(H)O^3$, lantanuric acid.
H.HO, water . . . . . $C^3N^2H^3(HO)O^3$, oxaluric acid.
H.H²N, ammonia . . . . $C^3N^2H^3(H^2N)O^3$, oxaluramide.

Tribromacetylurea, $C^3N^2H^3Br^3O^2 = CN^2H^3(C^2Br^3O)O$, is deposited from a solution of dibromobarbituric acid saturated with bromine, after standing for twelve hours, or more quickly on agitation, in colourless prismatic needles:

$$C^4N^2H^2Br^2O^3 + H^2O + Br = C^3N^2H^3Br^2O^3 + CO^2 + HBr.$$

The same compound is separated by chlorine from a solution of dibromobarbituric acid. It is sparingly soluble in cold water, easily soluble in alcohol; its vapour or powder strongly irritates the mucous membrane of the nose and eyes. It melts at 140°, without decomposition, to a colourless liquid, which solidifies at 123°; and when more strongly heated, gives off an oil (probably tribromacetamide), which solidifies on cooling, while cyanuric acid remains behind. Tribromacetylurea is decomposed by boiling with water, acids, or alkalis, yielding urea, carbonic acid, and bromoform, the formation of these products being, however, preceded by that of an intermediate acid, probably $C^3N^2H^3Br^3.H^2O$.—A solution of tribromacetylurea in ammonia becomes turbid immediately on boiling, with separation of bromoform; and the filtrate, when concentrated by evaporation, deposits long needles of isobiuret, $C^2N^3H^5O^2.H^2O$, which melts at 185° (biuret at 177°), but resembles biuret in other respects.

Monobromacetylurea, $C^3N^2H^5BrO^2 = CN^2H^3(C^2H^2BrO)O$, is obtained by mixing 3 pts. urea with 5 pts. bromide of bromacetyl, and recrystallising the product, from dilute alcohol, in needles, which dissolve sparingly in cold water, and are decomposed by water at the boiling heat, also by alkalis. Ammonia converts it into glycolylurea (hydantoin, iii. 177), or into oxacetylurea (glycoluric acid):

$$\underset{\text{Bromacetylurea.}}{CN^2H^3(C^2H^2BrO)O} = \underset{\text{Glycolylurea.}}{CN^2H^2(C^2H^2O)''O} + HBr.$$

$$\underset{\text{Bromacetylurea.}}{CN^2H^3(C^2H^2BrO)O} + H^2O = \underset{\text{Oxacetylurea.}}{CN^2H^3[C^2H^2(HO)O]O} + HBr.$$

2. *Oxalic Diureides.*—Allantoin and mycomelic acid are described in their alphabetical places.

Glycoluril, $C^4N^4H^6O^2$, is deposited in octahedral crystals, when a solution of allantoin, in about 30 pts. water, is acidulated with sulphuric acid, and treated with sodium-amalgam containing about 1 per cent. of sodium. It contains 1 at. oxygen less than allantoin. When boiled with baryta-water, it is resolved into glycoluric acid and urea (p. 960). (Rheineck.)

3. *Mesoxalic Monureides.*—The most important of these compounds appear to be alloxan and barbituric acid. **Alloxan**, the first discovered product of the artificial oxidation of uric acid, has recently been recognised by Liebig, as a pre-formed constituent of urine. When treated with bromine, it yields dibromobarbituric acid, convertible, by successive dehydrogenation, into bromobarbituric and **barbituric acid**, which last may be regarded as a sort of nucleus of the following series of compounds:

Mesoxalic Monureides.

$C^4N^2H^2(HO)^2O^3$ . . .	Alloxanic acid.
$C^4N^2H^2(Br^2)O^3$ . . .	Dibromobarbituric acid.
$C^4N^2H^4O^3$	Barbituric acid.
$C^4N^2H^3(Br)O^3$	Bromobarbituric acid.
$C^4N^2H^3(HO)O^3$ . . .	Dialuric acid.
$C^4N^2H^3(H^2N)O^3$ . . .	Uramile.
$C^4N^2H^3(H^2NSO^3)O^3$ . . .	Thionuric acid.
$C^4N^2H^3(NO)O^3$ . . .	Violuric acid.
$C^4N^2H^3(NO^2)O^3$ . . .	Dilituric acid.
$C^8N^4H^6(N^2O^5)O^6$ . . .	Violantin.

This last body, **violantin**, appears to be, not a residuary, but a completed compound of violuric and dilituric acids. The mutual relationship of barbituric acid, dialuric acid, and uramile in this subgroup, is strictly parallel to that of lantanuric acid, oxaluric acid, and oxaluramide in the oxalic group. Moreover, malonic and barbituric acids are homologous with oxalic and parabanic acids respectively.

Dibromobarbituric acid, or ***Bromalloxan***, $C^4N^2H^2Br^2O^3$. (Baeyer, Jahresb. 1863, p. 634; 1864, p. 632.)—This compound is produced by the action of bromine on violuric, dilituric, or hydurilic acid, according to the equations:—

$$\underset{\text{Violuric acid.}}{C^4N^2H^3(NO)O^3} + Br^4 = \underset{\text{Dibromobarbituric acid.}}{C^4N^2H^2Br^2O^3} + NOBr + HBr.$$

$$\underset{\text{Dilituric acid.}}{C^4N^2H^3(NO^2)O^3} + Br^4 = \underset{\text{Dibromobarbituric acid.}}{C^4N^2H^2Br^2O^3} + NO^2Br + HBr.$$

$$\underset{\text{Hydurilic acid.}}{C^8N^4H^6O^6} + H^2O + Br^6 = \underset{\text{Dibromobarbituric acid.}}{C^4N^2H^2Br^2O^3} + \underset{\text{Alloxan.}}{C^4N^2H^2O^4} + 4HBr.$$

To prepare it, hydurilic acid (iii. 220) is triturated to a paste with nitric acid; bromine is added as long as it is taken up, and the solution is warmed, whereupon it gives off nitrous acid, and deposits dibromobarbituric acid.

In this reaction the hydurilic acid is first converted into violuric or dilituric acid, which is then transformed into dibromobarbituric acid, as above.

This acid crystallises in colourless brilliant plates or prisms, belonging to the trimetric system. It is soluble in water, very soluble in hot alcohol and in ether. When boiled in aqueous solution, it is quickly decomposed into hydrobromic acid and alloxan; but it may be crystallised easily from nitric acid, which does not decompose it. It dissolves readily in alkalis, yielding compounds which are easily decomposed by heat, with loss of part of their bromine.

A solution of dibromobarbituric acid, digested with metallic *zinc*, loses half its bromine, and is converted into **bromobarbituric acid**, $C^4N^2H^3BrO^3$.

By *sulphydric acid*, in presence of water, it is reduced to dialuric acid:

$$\underset{\text{Dibromobarbituric acid.}}{C^4N^2H^2Br^2O^3} + H^2S + H^2O = \underset{\text{Dialuric acid.}}{C^4N^2H^4O^4} + 2HBr + S.$$

With a small quantity of *hydriodic acid*, it yields **hydurilic acid**:

$$\underset{\text{Dibromobarbituric acid.}}{2C^4N^2H^2Br^2O^3} + 6HI = \underset{\text{Hydurilic acid.}}{C^8N^4H^6O^6} + 4HBr + 3I^2;$$

but when it is heated with hydriodic acid in excess, the reduction proceeds a step further, and **barbituric acid** is produced:

$$\underset{\text{Dibromobarbituric acid.}}{C^4N^2H^2Br^2O^3} + 4HI = \underset{\text{Barbituric acid.}}{C^4N^2H^4O^3} + 2HBr + 2I^2.$$

A solution of dibromobarbituric acid, saturated with bromine, deposits crystals of tribromacetyl-urea (p. 960).

Barbituric acid, $C^4N^2H^4O^3.2H^2O$, crystallises in beautiful prisms, or sometimes in plates or needles, belonging to the trimetric system, sparingly soluble in cold, easily in hot water. By *fuming nitric acid*, it is converted into dilituric acid (ii. 965); by *potassic nitrate* into potassic violurate; and by *bromine*, into dibromobarbituric acid.—When boiled with caustic *potash*, it gives off ammonia, and yields malonate of potassium, $C^3H^2K^2O^4$, whence it appears to have the constitution of malonyl-urea:

$$CN^2H^2(C^3H^2O^2)''O \;=\; \underset{\text{Malonic acid.}}{C^3H^4O^4} + \underset{\text{Urea.}}{CN^2H^4O} - 2H^2O.$$

Barbituric acid is dibasic, and forms chiefly acid salts, which are obtained by treating the corresponding acetates with barbituric acid. The neutral lead-salt is obtained by precipitation with neutral lead-acetate. The following have been analysed:

Barbiturate of	Ammonium .	$C^4N^2H^3(NH^4)O^3$.
„	Potassium . .	$C^4N^2H^3KO^3$.
„	Sodium . .	$C^4N^2H^3K^2O^3.2H^2O$.
„	Barium . .	$C^8N^4H^6Ba''O^6.2H^2O$.
„	Copper . .	$C^8N^4H^6Cu''O^6.3H^2O$.
„	Lead. . .	$C^4N^2H^2Pb''O^3$.

Dibarbituric acid, $C^8N^4H^6O^5 = 2C^4N^2H^4O^3 - H^2O$.—The ammonium-salt of this acid is formed by heating barbituric acid with glycerin to 150°. The acid itself is separated by hydrochloric acid from its potassium-salt, as a white nearly insoluble powder. It is dibasic, and its acid salts are sparingly soluble in water, and mostly amorphous. The neutral dibarbiturates of alkali-metal are easily soluble in water, and are precipitated by alcohol.

Dibarbituric acid, treated with bromine and water, is transformed into yellow crystals of hydrobromate of dibromodibarbituric acid, $C^8N^4H^4Br^2O^5.HBr$, which, in contact with water or alcohol, are converted into white crystals of dibromodibarbituric acid, $C^8N^4H^4Br^2O^5$; this acid crystallises from hot water in large colourless crystals containing 1 at. water.

4. *Mesoxalic Diureides.*—The relationship between the three mesoxalic diureides—hypoxanthine, or sarcine, $C^5N^4H^4O$; xanthine, $C^5N^4H^4O^2$; and uric acid, $C^5N^4H^4O^3$—though long suspected, from the similarity of their formulæ, has but recently received an experimental demonstration at the hands of Strecker and Rheineck. These chemists have shown that hypoxanthine is converted into xanthine (*q.v.*) by oxidation with nitric acid, and, conversely, that uric acid, by deoxidation with sodium-amalgam, yields a mixture of xanthine and hypoxanthine. Xanthine is doubtless a monureide of barbituric and a diureide of malonic acid, in the same sense that uric acid is a monureide of dialuric, and a diureide of tartronic acid.

Pseudo-uric and uroxanic acids have the composition of hydrates of uric acid. Uroxanic acid, $C^5N^4H^{10}O^6 = C^5N^4H^4O^3.3H^2O$, is actually produced by the fixation of water on uric acid, its potassium-salt being formed by boiling uric acid for a long time in potash-ley. Pseudo-uric acid, $C^5N^4H^6O^4 = C^5N^4H^4O^3.H^2O$ (iv. 744), is not produced by direct oxidation of uric acid, but results from the combination of cyanic acid vapour with uramile or amidobarbituric acid, $C^4N^2H^3(H^2N)O^3$ (p. 961). For just as cyanic acid converts ammonia into anomalous cyanate of ammonia, or urea, so does it convert the residue of ammonia contained in uramile, into a residue of urea, thereby changing the amido-monureide into a simple diureide, thus:

$$\underset{\text{Uramile.}}{C^4N^2H^3(H^2N)O^3} + \underset{\text{Cyanic acid.}}{CNHO} \;=\; C^4N^2H^3(CN^2H^3O)O \text{ or } \underset{\text{Pseudo-uric acid.}}{C^5N^4H^6O^4}.$$

URINARY CALCULI.
URINARY PIGMENTS. } See the next article.
URINARY SEDIMENTS.

URINE. The secretion of the kidneys, the chief fluid excretion of man and of the higher animals. The healthy urine of man is a clear, yellowish, fluorescent liquid, of a peculiar odour, saline taste, and acid reaction, having a mean specific gravity of 1·020, and generally holding in suspension a little mucus.

Normal Constituents.—1. Water.—2. *Inorganic salts*: potassium, sodium, ammonia, calcium, magnesium, in combination with hydrochloric, phosphoric, sulphuric (nitric, carbonic) and silicic acids. The ash contains iron.—3. *Nitrogenous crystalline bodies*: urea, uric acid, hippuric acid, creatinine, xanthine (ammonia).—4. *Non-nitrogenous organic bodies*: sugar (in minute quantities, Brücke, Bence-Jones); lactic, succinic, oxalic, formic (malic), and phenylic acids. All these are found in small quantities; indeed, their normal occurrence can hardly be said to be certain.—5. *Free gases*: oxygen, nitrogen, carbonic acid. In 100 c.c. of urine, Planer found 0·87 N, 0·06 O, 4·54 free CO^2, 2·07 fixed CO^2, measured at 0° C., and 760 mm.

6. *Pigments.*—Several substances have been described, by various observers, as urinary pigments. Scherer (Ann. Ch. Pharm. lvii. 180), by decomposing, with hydrochloric acid and alcohol, the precipitates formed in urine by neutral and basic acetate of lead, obtained colouring bodies of variable composition. Harley (Wurt. Verdhl. v. 1) has given the name *urohæmatin* to a dark-red, amorphous, resinous substance, containing iron, readily soluble in alcohol, ether, fresh urine, and alkalis, but insoluble in water or acids, which he obtained from urine.—According to Thudichum (Brit. Med. Journ. Nov. 5, 1864), there is but one normal urinary pigment, *urochrome*, an amorphous substance, of a pure yellow colour, easily soluble in water, less so in ether, very dilute acids, and alkalis, and least of all in alcohol.—Schunk (Proc. Roy. Soc. xv. 1) believes that human urine contains two peculiar and distinct extractive matters (pigments), one soluble in alcohol and ether, of the composition $C^{68}H^{31}NO^{62}$; the other soluble in alcohol, but insoluble in ether, and of the composition $C^{38}H^{27}NO^{28}$: he regards the results of previous observers as being the products of greater or less decomposition.

In various diseases spontaneously occurring deposits of urates are often highly coloured of a red or rose-red hue. The pigments in such cases, known under the names of *rosacic acid*, *purpurin*, *uroerythrin*, have at present been little studied. The urine of man and of many animals (dog's urine contains a very large quantity) contains in health a small quantity, and in some cases of disease a very large amount, of a substance which was called by Heller *uroxanthin*, but which has been shown by Schunk to be *indican*. Fresh urine is precipitated with neutral and basic acetate of lead, the filtrate treated with ammonia, and the resulting precipitate washed, suspended in alcohol, and submitted to sulphuretted hydrogen. The filtered alcoholic solution is evaporated at a low temperature. It may be further purified by dilution with water, agitation with fresh hydrated oxide of copper, filtration, treatment with sulphuretted hydrogen, and renewed filtration. By the action of acids, indigo-blue and indigo-red, with which most probably the *uroglaucin* and *urorhodin* of Heller are respectively identical, may be obtained. The same change probably takes places through the natural decomposition of urine under certain conditions, for indigo-blue has been observed to occur spontaneously in urine on exposure to air. (Hassall.)

Harley regards all these matters as derivatives from his urohæmatin. Thudichum denies the existence of indican, and states that his urochrome yields, under various processes of decomposition, a black or brown powder, *uromelanin* (and a red resin), the latter consisting mainly of *uropittin*, insoluble, and *omicholic acid* (Scharling's omichmyl-oxide), soluble in ether,—and passes by a simple process, probably of oxidation, into uroerythrin. Hassall, however, was able to convert the blue pigment into isatin and aniline, and Schunk states that both the brown powder and resin are products from indican.

7. *Albuminoïd Matters and Ferments.*—If urine be mixed with four or five times its bulk of spirit, and a watery extract be made of the resulting deposit, a solution is obtained which is not precipitated by nitric acid, and which, on boiling, gives a precipitate of phosphates only, but, especially when concentrated by evaporation, shows the xanthoproteic and Millon's reactions very distinctly. The same solution rapidly converts starch into sugar. By treating urine with phosphate of calcium (see PEPSIN, SALIVA), ferments may be obtained capable of acting on starch, and of digesting albuminoïd matters.

8. *Extractives and other Matters.*—Colloïd acid of Marcet (Proc. Roy. Soc. xiv. 1). Decolorised urine is concentrated, treated with baryta, filtered, dialysed for 40 hours, again concentrated, and treated with basic acetate of lead, avoiding an excess. The lead-salt thus obtained may be decomposed with sulphuric acid. Schönbein is led to believe that urine normally contains a trace of peroxide of hydrogen. Urine is said to contain unoxidised sulphur and phosphorus.

Occasional or Abnormal Constituents.—*Blood*, the corpuscles being either entire and forming a sediment, or destroyed, and their hæmoglobin altered. *Pus*, *mucus*, *spermatic fluid*, &c. *Albumin*. In most instances the albumin of albuminous urine seems to be identical with serum-albumin. In some cases heat alone, in other cases nitric acid alone, fails to produce a precipitate. In a case of *Mollities ossium*, Bence-Jones found in the urine a peculiar protein-substance, which was coagulated by nitric acid in the cold, but redissolved on applying heat, reappearing, however, on cooling. *Fibrin* in bloody, and especially in the so-called "chylous" urine. *Casein*, or alkaline albuminates. *Fats*, *cholesterin*. *Leucine*, *tyrosine* (in certain hepatic diseases). *Allantoin* (in young children). *Cystine*, *xanthine*, *taurine*. *Glucose* (in diabetes and in smaller quantities in various chronic diseases). *Inosite*, *acetone*, *alkapton*, *lactic, acetic* (?), *metacetonic* (?), *butyric, valerianic* (?), *benzoic, succinic, oxalic, oxaluric, taurocholic, glycocholic, cholic acids. Biliary pigments, indigo-blue, melanin.*

These are products of metamorphosis; but the urine is also frequently the bearer of matters derived directly from the food. Of the substances which are capable of being absorbed from the alimentary canal into the blood, some reappear in the urine unchanged, while others are more or less altered, the changes being, with some exceptions, those of oxidation. Thus, there have been recovered from urine (in most instances, of course, in small quantities) arsenic, antimony, bismuth, copper, chromium, gold, iron, lithium, lead, mercury, silver, tin, zinc. The following substances also are said to pass unchanged:—alkaline carbonates, sulphates, nitrates, phosphates, borates, chlorates, silicates, chlorides, iodides, bromides; salts of calcium, magnesium, and barium; sulphocyanate and ferrocyanide of potassium; urea, leucine, hippuric acid, creatine, quinine (?), morphine, strychnine, atropine, alcohol (?), sulphovinates, sulphomethylates, sulphoamylates; gallic, pyrogallic, anisylic, cumaric, cuminic, camphoric, and piric acids, together with several pigmentary and odoriferous matters. The ammonia-salts pass unchanged, or are partially converted into nitrates. Free organic acids (oxalic, citric, &c.) are unchanged; their neutral salts, however, are converted into carbonates; malic acid, as malate of calcium, becomes succinic acid (Meissner). Sulphur and alkaline sulphides and sulphites are changed, in part at least, into sulphates. Sulphur taken in by the skin is said to give rise to xanthine. Free iodine becomes alkaline iodide. Tannic is changed into gallic acid. Benzoic acid, hydride of benzoyl, cinnamic acid, quinic acid, and mandelic acid give rise to hippuric acid. Nitrobenzoic acid is converted into nitrohippuric acid, chlorbenzoic into chlorhippuric, salicylic into salicyluric, toluic into toluric, anisic into anisuric acid. Uric acid, allantoin, alloxantin, guanine, glycocine, theine, and theobromine are said to give rise to an increase of urea. Salicin is converted into salicylol, salicylic acid (salicyluric), and saligenin. Ferrocyanide of potassium becomes ferricyanide. Indigo-blue is said to be reduced to indigo-white.

Acidity of Urine.—Healthy urine has generally when passed an acid reaction; the mean amount of acidity may be taken as equivalent to 2 grms. of oxalic acid in the 24 hours. The degree of acidity varies from time to time; it is lessened during digestion; indeed the urine may, after a meal, become alkaline. The acidity is due, in part at least, to the acid phosphate of sodium, but the quantity of that salt present in healthy urine is insufficient to account for the whole of the acidity; the rest is supplied by some free acid or acids—hippuric, lactic, colloïd. According to Scherer, the acidity of urine exposed to the atmosphere gradually increases for several days, through an "acid fermentation," in which the mucus and the pigmentary and extractive matters take part; afterwards a species of yeast appears. This increase of acidity is, however, denied by Bence-Jones.

Alkaline Urine.—Sooner or later, within a few days, or not until two or three weeks, the acid gives way to an alkaline reaction, the urea becoming converted into carbonate of ammonia through a process of fermentation. This change is accompanied by the appearance of crystals of triple phosphate, confervoïd growths, and vibriones. It may take place almost immediately after the urine has been passed, or (in certain diseases) even within the bladder. The mucus has been supposed to act as a ferment; but this is probably incorrect. It is much more likely that the change is due to the action of a distinct ferment, perhaps an organic being.

Table (after **Parkes***) of the Amounts of the several Urinary Constituents passed in Twenty-four Hours.*

	By an average man of 66 kilos.		Per 1 kilo. of body-weight.	
Water	1501·00	centimetres.	23·000	centimetres.
Total solids	61·14	grammes.	·93	grammes.
Urea	33·18		·500	
Uric acid	·555		·0084	
Hippuric acid (Bence-Jones)	·4		·006	
Creatinine (Neubauer)	·91		·014	
Pigment and extractives	10·00		·151	
Sulphuric acid	2·012		.0305	
Phosphoric acid	3·164		·048	
Chlorine	(8·21) 7·00		·126	
Ammonia	·77			
Potassium	2·5			
Sodium	11·09			
Calcium	·260			
Magnesium	·207			
Iron				

Urine, being the vehicle through which the body gets rid of by far the greater part of the solid matters resulting from or concerned in the vital processes of metamorphosis, naturally varies within the widest limits, as to both the absolute and relative quantities of its constituents, according to the condition, behaviour, and treatment of the organism. The amount of urea passed during a given time is, taken relatively to the body-weight, increased in childhood and lessened in old age; it is directly dependent on the quantity and quality of food consumed, and is obscurely connected with the labours of the frame (see NUTRITION, iv. 153). The uric acid is increased by food (especially by animal food), by exercise, by hindrances to the action of the skin, or to the function of respiration in general, and by various morbid conditions. Hippuric acid is increased by vegetable food; in the horse it is said to be increased by work. Creatinine is increased by animal food. The chlorides, sulphates, and phosphates vary with the food; the sulphates and phosphates are said to run, to some extent, parallel with the urea, and to be increased by muscular work, and the phosphates (especially the earthy phosphates) by mental labour. For further details consult Parkes, "The Composition of the Urine in Health and Disease."

Urine of other Animals.—The urine of carnivora in general is acid and clear, contains a large amount of urea, but only a small quantity of uric acid. That of herbivora is alkaline and turbid (from carbonates), contains hippuric but no uric acid (unless the animals are starving or feeding on flesh), a large quantity of earthy carbonates, and but little phosphates. The urine of the dog is wholly or very nearly free from uric acid; contains cynurenic acid, hippuric acid, a large quantity of indican; and, when the animal is feeding on flesh and fat, some succinic acid. That of the horse is rich in hippuric acid and earthy carbonates, and contains a decided quantity of sugar. That of the cow contains from ·4—2·7 per cent. of hippuric acid (Henneberg); from it have been obtained damolic, damaluric, and taurylic acids. The urine of the sucking calf is remarkable for the presence of allantoin and the absence of hippuric acid, a feature which disappears on weaning. The urine of the pig is alkaline, and rich in alkaline carbonates, clear even on standing for some time, but becomes turbid when heated, contains urea, but neither uric nor hippuric acid. The portion of the excrement of birds that corresponds to urine is rich in uric acid and urates of ammonia and lime. Urea is said to exist in the excrement of carnivorous birds. The urine of ophidians consists of uric acid, urates of sodium, potassium, and ammonium, some urea, and a little calcic phosphate. The urine of the *Testudo tabulata* contains urea, uric and hippuric acids, chlorides, sulphates, and a small quantity of phosphates. The urine of the frog contains urea, chlorides, and phosphates. Uric acid has been found in the excrement of butterflies, beetles, caterpillars, and snails, and guanine in the excrement of spiders, and in certain organs of mollusca.

Urinary Sediments.—Many specimens of urine exhibit, on standing, deposits or sediments consisting of morphological elements, and of chemical bodies, crystalline or amorphous. To the first class belong blood-corpuscles, pus- and mucus-corpuscles, spermatozoa, epithelial scales, casts of the uriniferous tubes, &c. The members of the second class are various and many.—*Urates* (the ordinary brick-dust sediment) in amorphous irregular particles, round globules, and fine acicular crystals, consisting of a great excess (82 per cent.) of uric acid in combination with variable quantities of ammonia, soda, potash, and lime.—*Uric acid*, in crystals of various shapes, mostly coloured, chiefly rhombic prisms and plates, sometimes thin hexagonal plates, dumb-bells (artificial only?).—*Phosphates*: ammonio-phosphate of magnesium, in large, transparent, rhombic prisms, or penniform; phosphate of calcium, amorphous, or crystallising in very various shapes, often forming glomerules or rosettes, with lozenge-shaped or acicular elements, sometimes penniform.—*Oxalate of calcium*, in octahedral crystals, or forming the "dumb-bell" bodies.—*Carbonate of calcium* occasionally occurs in man, sometimes in the form of dumb-bells. It is very abundant in the urine of the horse, in peculiar globular bodies, formed of concentric layers.—*Hippuric acid* (uncommon), in acuminated needles or acicular crystals.—*Cystine*, amorphous, or in transparent, colourless, hexagonal plates.—*Leucine*, in peculiar round bodies, having a concentric arrangement, or in needles, or granular.—*Tyrosine*, in acicular heaps and rosettes.—*Xanthine*, amorphous, or in small oblong plates (Bence-Jones).—*Cholesterin.*—*Sulphate of calcium*, in acicular crystals, has been observed. (Valentiner.)

Urinary Calculi.—In the pelvis of the kidney, in the ureters, in the bladder, and in the urethra are found concretions of very variable size, form, consistency, structure, and composition. They are called *urinary* (*renal*, *ureteric*, *vesical*, *urethral*) *calculi*, and are made up chiefly of the solid constituents of the urine. Sometimes homogeneous, they are more frequently formed of numerous concentric layers. A central portion, the *nucleus*, may generally be distinguished from the external portions, and is sometimes formed by a foreign body.

Uric acid, urates of ammonium, calcium, potassium, sodium, and magnesium, phosphates of calcium, of ammonium and magnesium, and of iron, carbonates of calcium and magnesium, oxalates of calcium and ammonium, hippurate of ammonium, chloride of ammonium, cystine, xanthine, ferric oxide, silica, mucus, fat, blood, colouring and other extractive matters, have all been mentioned as constituents of urinary calculi. It is very unusual to meet with calculi formed exclusively of a single substance; many calculi are formed chiefly of uric acid, others chiefly of oxalate of calcium, but these generally contain at least a small quantity of other matters. The most common forms are uric acid with urates of ammonium or calcium, ammonio-magnesian phosphate with phosphate and carbonate of calcium, uric acid with phosphates, oxalate of calcium with phosphates. The concentric layers are frequently distinct, not in appearance only, but also in composition; and a curious alternation of material is at times observed, uric acid, for instance, changing place with urates, phosphates, oxalates, &c. A nucleus of uric acid is frequently surrounded by an external coat of phosphates, but a nucleus of phosphates with a coating of uric acid, &c., is never observed. The most external layers in many calculi of various composition is apt to be phosphatic. The oxalate calculi (often called *mulberry*, from their peculiar form) are generally the hardest, the phosphatic the softest. Calculi of cystine are rare, those of xanthine still more so.

The following may be taken as analyses of the more typical forms:

Uric acid.

Uric acid	92·8	84·69
Urates	3·2	9·03
Ammonio-magnesian phosphate		1·12
Extractives	1·00	2·61
Water	3·00	

Phosphatic.

Urate of sodium . . .	9·77
Calcic phosphate . . .	34·74
Ammonio-magnesian phosphate	38·35
Calcic carbonate . . .	3·14
Magnesic carbonate . .	2·55
Extractives, &c. . . .	6·87

Oxalate.

Calcic oxalate . .	63·5
Calcic phosphate . .	6·2
Water and organic matters	30·3

Analysis of Urine.

Determination of Urea. (Liebig's method.) *Prepared urine* (if albumin be present it must be separated by boiling; some urea will probably be lost): two volumes of urine are mixed with 1 volume of a "baryta mixture" (consisting of 2 volumes of baryta-water to 1 volume of a solution of barium-nitrate, both saturated in the cold), and filtered.—*Urea-solution*: 2 grms. of pure urea are dissolved in water, and the solution diluted to 100 c.c.—*Mercurial solution*: a concentrated solution of pure mercuric nitrate is diluted with four times its bulk of water. 10 c.c. of the urea-solution are measured into a beaker, and the mercurial solution is slowly added from a burette as long as any precipitation takes place; a drop of the mixture is then let fall by a glass rod into a drop of a solution of sodic carbonate, placed in a watch-glass, or on a glass plate, over some black surface. If the precipitate, which occurs on the mingling of the two drops, does not become in a few seconds distinctly yellow, more of the mercurial solution must be added to the mixture in the beaker, and the trial made again. As soon as a distinct yellow colour appears (the shade being noticed by the observer in order to guide him afterwards), the trial drops are returned into the beaker, and a little of the soda-solution added, until the mixture is only faintly acid. A drop is then again to be tried with the soda-solution; and if the yellow colour does not show itself, a small quantity of the mercurial solution must still be added to the mixture in the beaker, and trial made again. When the yellow colour has been thus obtained, the total quantity of mercurial solution used is read off; it corresponds to ·2 grm. urea. The mercurial solution itself is then diluted according to these results, so that 20 c.c. of it corresponds to 10 grms. of the urea-solution, *i.e.* so that 10 c.c. correspond to ·1 grm. urea. It is well not to add, at once, the whole of the water required; but to stop a little short of that, and titrate again, since, practically, the degree of dilution required is rather less than that suggested by calculation.

Method.—Of the prepared urine, 15 c.c., corresponding to 10 c.c. of the original urine, are poured out into a beaker or flask, and the mercurial solution is added until the yellow reaction, as described above, is obtained; the mixture is also in the same way reduced in acidity, and trial made again. The quantity of mercurial solution used will give the amount of urea in the 10 c.c. of urine. Unfortunately, the reaction is exact only for fluids containing 2 per cent. of urea; its appearance is premature when more, and is delayed when less than that percentage is present. If the prepared urine contains an excess of urea, double its volume of the mercurial solution will have been used, and yet no reaction set in. Hence, if, on arriving at this point, 1 c.c. of distilled water be added to the mixture for every additional 2 c.c. of the mercurial solution employed, the proportion of urea will be maintained at 2 per cent., and the final result will be correct. Thus if, after the addition of 30 c.c. of the mercurial solution to 15 c.c. of prepared urine, the reaction is not seen, 1 c.c. of distilled water is added, and the process continued. Supposing the reaction finally sets in when 10 c.c. more, or 40 c.c. in all, of the mercurial solution have been used, the 5 c.c. of distilled water, which have been also added, will bring up the original 15 c.c. of urine to 20 c.c.; the 40 c.c. of mercurial solution will have been employed on a fluid containing 2 per cent. of urea. If the prepared urine contains less than 2 per cent. of urea, an approximate correction may be made by subtracting ·1 c.c. from every 5 c.c. of the mercurial solution that is run short of the normal 30 c.c. Thus, if with 15 c.c. of prepared urine, the yellow colour is struck on using 20 c.c. of the mercurial solution, ·2 c.c. $(30-20=5\times 2)$ are deducted, and therefore 19·8 c.c. taken as the correct result. A further correction must be made for chloride of sodium, the presence of which delays the reaction. We may make an approximate correction by deducting from the quantity of mercurial solution employed 1·5 c.c.—2·5 c.c., according to the quantity of chloride of sodium present. Or we may first remove the chloride. To 15 c.c. of prepared urine, one or two drops of solution of neutral chromate of potash are added, and a solution of nitrate of silver dropped in from a burette, until the appearance of the red chromate of silver indicates that the whole of the chloride has been thrown down; the mercurial solution can then be at once used without removing the silver-precipitate. The reduction in the percentage of urea, by the addition of the silver-solution, must of course be taken into account. Or two portions of prepared urine may be taken of 15 c.c. each. One is neutralised with nitric acid, the mercurial solution added, and the point marked at which a permanent precipitate (a distinct cloud, not a mere opalescence) is produced. The other is titrated in the usual way. The number of c.c. employed in the latter, minus those employed in the former operation, will give the real quantity of urea. It must be remembered that other nitrogenous bodies, creatinine, allantoin, &c., are precipitated by the mercurial solution in the same way as urea.

Heintz and Ragsky's Method.—A given quantity (20 c.c.) of urine is precipitated with tetrachloride of platinum, and the precipitate washed with spirit, dried, and weighed. From 2 to 5 c.c. of the same urine (according to concentration) are heated to 180°—200°, in a covered platinum or porcelain capsule, with an equal bulk of sulphuric acid; and after cooling are diluted with water, filtered, and precipitated with tetrachloride of platinum. Both precipitates are calculated for 100 c.c. urine, and the former deducted from the latter; the result multiplied by ·13423 gives the percentage of urea.

Davey's Method.—A small quantity of urine is poured into a graduated glass tube a third full of mercury; the tube is then filled with a solution of sodic hypochlorite, rapidly inverted over a saturated solution of chloride of sodium, and left to stand several hours. The quantity of gas (nitrogen) given out is read off. 1·549 cubic inches of nitrogen at 60° F. and 30″ bar. = 1 grain urea.

Uric acid, ammonia, &c. are in this method confounded with urea.

Bunsen's Method.—A given quantity of prepared urine is heated, at 220°—240°, with chloride of barium in a sealed tube, and the resulting carbonate of barium determined. 1 grm. barium-carbonate = ·4041 urea.

Uric Acid.—To 200 c.c. of urine, 10 c.c. of hydrochloric acid are added, the mixture allowed to stand 48 hours in a cool place, filtered through a very small filter, on which the crystals are placed, washed, dried, and weighed. The wash-water should not exceed 30 c.c.; if the last drops still produce cloudiness in a silver-solution, more must of course be used; and for every *additional* cubic centimetre of wash-water used, ·045 milligramme is added to the amount of uric acid found. This correction is a compromise between the loss arising from the partial solubility of the uric acid, and the gain due to the colouring-matter inseparably connected with the crystals. Hassall (Lancet, 1867, May 6), has shown that the mixture of uric acid and pigment, which is usually weighed as uric acid, varies extremely, according to the concentration of the urine, the amount of acid employed, the time allowed for crystallisation, and the surrounding temperature. If the urine contains albumin, this must first be removed by coagulation, with the very careful use of dilute acetic acid, using afterwards strong acetic, instead of hydrochloric, acid to precipitate the uric acid.

Hippuric Acid.—The urine is digested with animal charcoal (2 grammes to each 10 c.c.), and filtered; 200 c.c. are evaporated down to 50 c.c., 20 c.c. of hydrochloric acid added, and the mixture allowed to stand for twenty-four hours in a cool place. The hippuric acid which crystallises out is collected on a weighed filter, washed with a small quantity of cold water until the filtrate is colourless, dried at 100°, and weighed. The wash-water is collected and measured, and for every 6 c.c. of it, ·01 gramme is added to the weight of hippuric acid, in order to correct the error due to that substance being slightly soluble in cold water. This process is of course useless where uric acid is present.

Creatinine.—To 300 c.c. of urine, rendered alkaline with milk of lime, a solution of calcic chloride is added as long as any precipitate occurs. The mixture is allowed to stand for one or two hours, and filtered. The filtrate and washings are evaporated to dryness in a water-bath, and, while still warm, treated with 30 or 40 c.c. of alcohol, 95 per cent. The mixture, after standing for four or five hours in a cool place, is passed through a small filter, and the filter washed with small quantities of spirit.

The filtrate and washings—reduced in bulk, if necessary, to 40 or 50 c.c. by being placed over hot plates—are mixed with 5 c.c. of a solution of chloride of zinc (specific gravity 1·2, absolutely free from acidity), and allowed to stand for three or four days in a very cool place. The crystals that appear are collected on a small filter, washed first with the mother-liquor, and then with small quantities of spirit, dried at 100°, and weighed. 100 pts. of zinc-compound = 62·44 pts. of creatinine.

Albumin.—From 30 to 100 c.c. of urine, according to concentration, are heated with the naked flame, a drop or two of acetic acid being added, until the albumin is thoroughly coagulated, and the fluid capable of being filtered. The deposit is dried at 120°, and over sulphuric acid, until it ceases to lose weight. Other matters are carried down with the albumin, but these are insignificant.

Sugar.—In diabetes, when the quantity of sugar is very considerable, the determination may be made with the alkaline copper-solution, by the saccharimeter, or by fermentation. When the quantity of sugar is very small, the following process may be adopted:—A given quantity of urine (1000 cubic centimetres) is concentrated, and precipitated with sugar of lead and filtered; the filtrate is precipitated with acetate of lead and filtered. This second filtrate is precipitated with ammonia, the deposit suspended in alcohol, submitted to sulphydric acid, and filtered. The spirit filtrate is evaporated, and its sugar determined in any of the usual ways.

Chlorides.—In fresh urine, free from albumin, much uric acid, or mucus, the chlorides may be determined with tolerable accuracy by the silver and chromate of potash method.

Phosphates may be determined by the uranic oxide process.

Ammonia.—Twenty cubic centimetres of urine are placed in a shallow vessel, over which is arranged another small shallow vessel containing 10 c.c. of a standard solution of dilute sulphuric acid; and the whole is covered with an airtight bell-jar. The bell-jar is slightly raised, 10 c.c. of milk of lime quickly introduced into the urine, and the jar at once replaced. In about 48 hours, the whole of the ammonia is disengaged from the urine, and absorbed by the sulphuric acid. By titrating the sulphuric acid after the experiment, and comparing it with the standard solution, the amount of ammonia is arrived at.

Bile Acids.—Urine is precipitated with basic acetate of lead and a little ammonia; the precipitate is washed, boiled in alcohol, and filtered hot; the alcoholic solution is treated with a few drops of soda, and evaporated to dryness; the residue extracted with absolute alcohol; the filtered solution reduced in volume, mixed with an excess of ether, and left to crystallise. The crystalline deposit is mixed with dilute sulphuric acid (1 to 4), and a few drops of a solution of cane-sugar added. The mixture, on being gently warmed, should give the purple coloration of Pettenkofer. M. F.

URINE, FUSIBLE SALT OF. *Sal urinæ fusibilis.*—Ammonio-sodic phosphate.

URINE, SPIRIT OF. The solution of ammonium-carbonate, obtained by distilling putrid urine.

UROCHROME, UROCYANIN, UROERYTHRIN, UROGLAUCIN, UROHÆMATIN, UROMELANIN, UROPITTIN, URORHODIN. See URINARY PIGMENTS (p. 963).

UROSTEALITE (from *οὖρον*, urine; *στέαρ*, tallow; and *λίθος*, stone).—A fatty substance found in a urinary calculus. On evaporating the solution of the calculus in carbonate of sodium, adding a little sulphuric acid, extracting with ether, and leaving the ether to evaporate, the urostealite was obtained as a violet residue, which softened in boiling water without dissolving, was sparingly soluble in alcohol, more easily in ether and in caustic potash, less easily in ammonia and in carbonate of potassium. It softened when heated, and when more strongly heated gave off a thick smoke, and an odour like that of benzoin and shellac. (Heller, Arch. f. Phys. u. pathol. Chemie, u. Mikros. 1845, p. 1.)

UROXANIC ACID. $C^5N^4H^{10}O^6$. (Städeler, Ann. Ch. Pharm. lxxviii. 286; lxxx. 119.)—A product obtained by boiling uric acid with rather strong potash-ley:

$$\underset{\text{Uric acid.}}{C^5N^4H^4O^3} + 3H^2O = \underset{\text{Uroxanic acid.}}{C^5N^4H^{10}O^6}.$$

Other products are formed at the same time—namely, lantanuric acid, urea, formic acid, and oxalic acid.

On leaving the resulting solution in contact with the air, it absorbs carbonic acid, and slowly deposits acid urate of potassium in the form of a white powder; but, after several weeks or months, tabular crystals of potassic uroxanate are formed, the urate disappearing at the same time. By decomposing the solution of the uroxanate with hydrochloric or sulphuric acid, the uroxanic acid is obtained in indistinct prismatic crystals, or from warm moderately dilute solutions, in colourless transparent tetrahedrons.

Uroxanic acid is slightly soluble in cold water, quite insoluble in cold alcohol. It is easily decomposed even by boiling with water, giving off carbonic anhydride. The dry acid heated in a glass tube above 100°, gives off water and carbonic anhydride. If, however, the temperature be maintained at 130° till the weight of the residue becomes constant, the acid is found to have lost 34·8 per cent. of its weight, and a yellowish hygroscopic substance is left, called uroxil by Städeler, and having the composition of uroxanic anhydride, $C^5N^4H^8O^5$ (which is also that of dialurate of ammonium). At a stronger heat, uroxanic acid melts to a brown liquid, gives off ammonia, and probably also cyanide of ammonium, yields an oily distillate solidifying as it cools, and leaves a small quantity of carbonaceous residue. Strong nitric acid does not act on uroxanic acid in the cold, but dissolves it when heated, without evolution of gas, the solution on cooling yielding crystals, probably a product of oxidation. The mother-liquor yields, on evaporation, a white residue, which is not coloured by carbonate of ammonium.

Uroxanic acid is dibasic, the general formula of its salts being $C^5N^4H^8M^2O^5$. Some of the uroxanates are soluble in water, but most of them are insoluble in alcohol.

The *ammonium-salt* separates, in small four-sided tablets, on adding alcohol to a solution of the acid in dilute ammonia.—The *potassium-salt*, $C^5N^4H^8K^2O^5.3H^2O$, obtained as above described from uric acid, crystallises in large, nacreous, four-sided plates, with angles of 97° and 83°. It is moderately soluble in cold, very soluble in hot water, insoluble in alcohol; gives off its water of crystallisation at 100°; and at a higher temperature melts, gives off a little carbonate of ammonium, and leaves a residue blackened by charcoal.

The *barium-salt* separates, on mixing a solution of the acid in excess of ammonia with chloride of barium, and adding alcohol, in thick flocks which gradually change to slender shining needles.—The *calcium-salt*, obtained in like manner, forms small, shining, four-sided plates, which, by boiling in the liquid, are converted into larger crystals, like those of the barium-salt.—The *lead-salt*, $2C^5N^4H^8Pb''O^5.H^2O$, is precipitated by nitrate of lead from the solution of the potassium-salt, in delicate satiny scales, quite insoluble in water, and becoming anhydrous at 100°.—The *silver-salt* is obtained in like manner, as a white flocculent precipitate, but soon settles down to a dense powder, which turns red on exposure to light, and black when heated in the liquid.

UROXANIC ANHYDRIDE. See preceding article.

UROXANTHIN. See Urinary Pigments (p. 963).

UROXIL. Syn. with Uroxanic Anhydride.

UROXIN. Syn. with Alloxantin (i. 138).

UROXYL. Syn. with Uroxil.

URSONE. $C^{10}H^{16}O$?—A resinous body obtained from the leaves of the red bearberry, *Arctostaphylos uva-ursi*. It was first prepared by Trommsdorff in 1854 (Arch. Pharm. [2], lxxx. 273), and further examined by Hlasiwetz (J. pr. Chem. lxiv. 123), who assigned to it the formula $C^{20}H^{17}O^2$. To prepare it, the leaves of the bearberry, after being freed from arbutin by exhaustion with water, are treated with alcohol, the solution is evaporated, the residue treated with water and ether, and the ursone which then remains undissolved, is purified by crystallisation from alcohol. Or the leaves are treated with ether in a displacement apparatus, whereby a dark-green extract is obtained, which deposits a considerable quantity of crystalline ursone to be purified by crystallisation from alcohol.

Ursone crystallises in slender colourless needles, having a silky lustre, tasteless and inodorous, insoluble in water and in aqueous acids or alkalis, soluble with difficulty in ether or alcohol. It melts at 190°—200°, and solidifies again in the crystalline form on cooling; if heated above its melting-point, it remains amorphous after cooling, and at a still higher temperature boils, and appears to volatilise without decomposition.

According to Hlasiwetz, ursone agrees in composition and in most of its properties with hartin from lignite (iii. 14).

URTICA. The stinging power of nettles, *Urtica urens* and *U. dioica*, is due (according to Saladin) to acid carbonate of ammonium, contained in glands beneath their epidermis; the juice contains nitrate of potassium and nitrate of calcium. According to Bollig, water distilled over the herb contains carbonate of ammonium; according to Gorup-Besanez, it contains formic acid.

The yellowish decoction of the leaves, when left to dry in contact with the air, especially in presence of alkalis, is said, by Leuch, to yield a fine emerald-green colour. The herb of *U. urens* yields, by fermentation, a so-called ferment-oil (ii. 636) (Bley). The seeds of both kinds of nettle are said to be useful as remedies in cases of dysentery.

The fibre of many species of *Urtica* yields useful tissues. The Chinese are said to fabricate a fine silky stuff from the fibres of *Urtica nivea*. (Handw. d. Chem. ix. 68.)

USNIC ACID, or **USNIN.** An acid obtained from several species of lichen. It was first prepared and examined by Knop (Ann. Ch. Pharm. xlix. 103), and further investigated by Rochleder and Heldt (*ibid.* xlviii. 12), Thomson (*ibid.* liii. 252), Stenhouse (*ibid.* lxviii. 97, 114), and Hesse (*ibid.* cxvii. 343).—Stenhouse assigned to it the formula $C^{38}H^{17}O^{14}$—more probably $C^{38}H^{16}O^{14}$, or $C^{19}H^{16}O^{7}$; according to Hesse, it is $C^{18}H^{18}O^{7}$. It is found in *Usnea florida*, *U. harta*, *U. plicata*, *U. barbata*, *Ramalina calicaris*, *Cladonia rangiferina*, *Parmelia furfuracea*, *Evernia prunastri*, and others.

According to Stenhouse, the several species of *Usnea* are best adapted for the preparation of usnic acid, especially *Usnea florida*; next in point of eligibility comes *Cladonia rangiferina*, while the several species of *Ramalina* and *Evernia prunastri* are less adapted for the purpose, because they yield resinous acids difficult to purify. Hesse uses *Ramalina calicaris* (var. *fraxinea* and *chnaumatica*) for the preparation of alpha-usnic acid, and *Cladonia rangiferina* for the preparation of beta-usnic acid.

Preparation.—Knop exhausts the lichens with ether in a displacement apparatus, then distils off the ether, and treats the residue with alcohol; the alcoholic solution thus obtained deposits usnic acid in crystals on cooling. Rochleder and Heldt digest the lichens with a mixture of ammonia and aqueous alcohol, filter the liquid after some minutes, then mix it with one-third of its volume of water, and neutralise with acetic acid; the usnic acid thereby precipitated is washed, and recrystallised from alcohol.—Stenhouse exhausts the lichens with milk of lime, and precipitates with hydrochloric acid.

Hesse also exhausts the lichens (*Ramalina calicaris*, var. *fraxinea* and *chnaumatica*) with milk of lime, supersaturates with hydrochloric acid, and boils for a short time, whereupon alpha-usnic acid crystallises out. The deposit is washed with water, then boiled with alcohol, and the residue is dissolved in boiling acetic acid, the solution mixed with animal charcoal, and filtered.—To prepare beta-usnic acid from *Cladonia rangiferina*, Hesse exhausts the lichen with dilute soda-ley; saturates with hydrochloric acid; washes the precipitate, which contains brown humous substances, with water; dries it, and exhausts it with ether; evaporates the ethereal solution; and mixes the residue with alcohol. Beta-usnic acid then crystallises out, and may be purified by recrystallisation from alcohol with addition of animal charcoal.

Properties.—Usnic acid forms thin, light, sulphur-yellow needles, which become strongly electric by friction, are not moistened by water, dissolve but sparingly in ordinary alcohol, even at the boiling heat, but easily in boiling ether or turpentine-oil.

Usnic acid melts when somewhat strongly heated, alpha-usnic acid at 203° (Hesse), at 200° (Knop); beta-usnic acid at 175°: this difference of melting-point is the only essential distinction between the two acids. Melted usnic acid is yellowish and resinous, and solidifies in the crystalline form on cooling; at a higher temperature it yields a crystalline sublimate, an oily distillate containing beta-orcein, and a carbonaceous residue. Usnic acid is not coloured by ferric chloride or by hypochlorite of sodium.

Chlorine converts usnic acid into a resinous body; *sulphuric acid* dissolves it, forming a yellow solution, which is precipitated by water. *Nitric acid* heated with it, forms a yellow resin. Usnic acid dissolves easily in *alkaline liquids*: the solutions, which contain beta-orcein together with a resin, become dark-red on exposure to the air, and at last nearly black.

Usnic acid is monobasic, the composition of its salts being $C^{18}H^{17}MO^{7}$, according to Hesse; $C^{19}H^{15}MO^{7}$, according to Knop. The usnates of the alkali-metals are soluble in water; the rest are insoluble in water, but soluble in alcohol; ether extracts usnic acid from them.

Usnate of ammonium, obtained by passing ammonia-gas into absolute alcohol in which usnic acid is suspended, forms needle-shaped crystals.—The *potassium-salt*, $C^{18}H^{17}KO^{7}.6H^{2}O$, is prepared by boiling usnic acid with a strong solution of potassic carbonate. It separates almost completely from the solution on cooling, and when recrystallised from alcohol, forms white laminæ, which give off all their water at 130°. Its solution froths like soap-water, and, when mixed with a large quantity of water. deposits an acid salt.—The *sodium-salt* forms stellate groups of silky needles; it reacts like the potassium-salt, but is more easily decomposed.—The *barium-salt*, $C^{36}H^{34}Ba''O^{14}$, may be crystallised from alcohol; the aqueous solution quickly becomes coloured on exposure to the air.—The *cupric salt*, $C^{36}H^{34}Cu''O^{14}$, is a green precipitate; the *lead-salt*, a white precipitate; the *silver-salt*, a white precipitate which quickly blackens.

UVITIC and **UVITONIC ACIDS.** Acids produced, according to Finck, by the action of baryta-water on pyroracemic acid. The former has the composition $C^{9}H^{8}O^{4}$; the latter appears to be merely a syrupy modification of pyroracemic acid (iv. 770).

UWAROWITE, *Chrome-garnet*, *Chrome-lime-garnet*, $3CaO.Cr^{2}O^{3}.3SiO^{2}$, with small quantities of alumina, ferrous oxide, and magnesia, occurs at Saranowskaja, near Bissersk, and near Kyschtimsk, in the Ural, in rhombic dodecahedrons, and massive, with imperfectly conchoïdal or splintery fracture, emerald-green colour, and greenish-white streak, vitreous lustre, more or less transparent on the edges. Hardness = 7·5 to 8·0. Specific gravity = 3·4 to 3·5. It does not fuse by itself before the blowpipe, but forms a clear olive-green glass with borax. (See GARNET, ii. 772.)

V

VACCINIC ACID. This name was given by Lerch (Ann. Ch. Pharm. xlix. 227) to a volatile acid, obtained on one occasion by the saponification of butter from cow's milk, but which appears to have been merely a mixture of butyric and cupric acids.

VACCINIUM. A small genus of plants including the bilberry and whortleberry. The green parts of the common bilberry (*Vaccinium Myrtillus*) contain quinic acid (Zwenger, Ann. Ch. Pharm. cxv. 108). The fruit contains, according to Fresenius (*ibid.* ci. 225):

Fruit-sugar	5·8	Soluble in water.
Free acid (regarded as malic acid)	1·3	
Albuminous substances	0·8	
Pectin, gum, colouring-matter	0·5	
Ash	0·8	
Kernel and husk	12·8	Insoluble in water.
Pectose	0·2	
Ash	0·55	
Water	77·5	

The colouring-matter of the berries forms with lead-oxide, a fine blue compound which is coloured green by alkalis. The berries yield, by fermentation, a kind of brandy ("Heidelbeerbrantwein" or "Heidelbeergeist") which is prepared in large quantities in many parts of the Black Forest.

Whortleberries, the fruit of *Vaccinium Vitis idæa*, and cranberries, the fruit of *Vaccinium Oxycoccus* (L.), *Oxycoccus palustris* (Rich.), contain, according to Scheele, citric acid and a small quantity of malic acid.

VACUUM. The most usual method of producing a vacuum, or rather a highly rarefied atmosphere, is by the common air-pump. The exhaustion may be made much more complete by filling the exhausted receiver with carbonic acid gas, absorbing this gas by lime, and repeating the process several times. A vacuum may also be produced by driving the air out of a vessel with steam, and then condensing the steam by cooling.

In the barometric or Torricellian vacuum, there is nothing present but a very minute quantity of mercury-vapour. An excellent method of producing a vacuum has been contrived by Dr. Sprengel (Chem. Soc. J. xviii. 9). It consists in connecting the vessel to be exhausted with the upper part of a long vertical tube, down which a column of mercury is made to flow.

VALENE. Syn. with VALERONE.

VALENCIANITE. A name given by Breithaupt to orthoclase from the silver-mine of Valenciana in Mexico; related to adularin, and containing, according to Plattner, 66·82 per cent. silica, 17·58 alumina, 0·09 ferric oxide, and 14·80 potash.

VALENTINITE. The trimetric variety of native antimonious oxide (i. 323).

VALERACETONITRILE. $C^{26}H^{48}N^4O^6$. (Schlieper, Ann. Ch. Pharm. lix. 16.)—A body containing the elements of 4 at. valeronitrile, C^5H^9N, and 3 at. acetic acid, $C^2H^4O^2$, or of 1 at. valeronitrile and 3 at. valeracetamide, $C^5H^{10}(C^2H^3O)NO$. It is found in the neutral oil produced by distilling glue with potassium-chromate and sulphuric acid, and is obtained therefrom, in the same manner as valeronitrile (ii. 272), by repeated fractional rectification of the portion boiling between 68° and 90°.

Valeracetonitrile is a mobile colourless liquid, moderately soluble in water, and miscible in all proportions with alcohol and ether. It has an aromatic odour, makes a transient grease-spot on paper, has a specific gravity of 0·79, and boils between 68° and 71°. It is very inflammable, and burns with a faintly luminous flame. By heating with sulphuric acid, or with aqueous fixed alkalis, it is decomposed, with formation of ammonia, acetic acid, and valerianic acid:

$$C^{26}H^{48}N^4O^6 + 8H^2O = 4C^5H^{10}O^2 + 3C^2H^4O^2 + 4NH^3.$$

Chlorine and bromine decompose valeracetonitrile, with evolution of hydrochloric or hydrobromic acid.

VALERAL. $C^5H^{10}O = \left.\begin{matrix}C^5H^9O\\H\end{matrix}\right\}$ or $\left.\begin{matrix}C^5H^9\\H\end{matrix}\right\}O$. *Valeraldehyde. Valerianic Aldehyde. Amylic Aldehyde. Valeryl-hydride.*—This body was discovered by Dumas and Stas (Ann. Ch. Phys. [2] lxxiii. 145), who obtained it by oxidising amylic alcohol with nitric or chromic acid. It is also produced in the distillation of fusel-oil with sulphuric acid (Gaultier, Ann. Ch. Pharm. xliv. 127); by the dry distillation of a mixture of formate and valerate of calcium (Limpricht, *ibid.* xcvii. 370); by the action of manganese-peroxide and sulphuric acid upon gluten (Keller, *ibid.* xxxii. 31); of chromic acid on castor-oil (Arzbächer, *ibid.* lxxiii. 202), and of sulphuric anhydride on leucine (Schwanert, *ibid.* cii. 226), in the dry distillation of valerates, most easily, according to Ebersbach (*ibid.* cvi. 262), from valerate of calcium after addition of lime; and, lastly, by the dry distillation of lupulin-resin which has been exhausted with water, after addition of lime. (Personne, J. Pharm. [3] xxvi. 241, 329; xxvii. 22.)

Valeral, obtained by the dry distillation of valerates, was formerly regarded as isomeric, but not identical, with valeraldehyde produced by oxidation of amylic alcohol; the two products, however, invariably exhibit the same reactions, and appear to differ only in boiling-point, that of the product obtained by distillation of valerates being somewhat the higher of the two, and not constant, a peculiarity doubtless arising from admixture of other substances.

Preparation.—Valeral is usually prepared by oxidising amylic alcohol with chromate of potassium and sulphuric acid. The best way of proceeding, according to Parkinson (Ann. Ch. Pharm. xc. 114), is to allow a mixture of 11 pts. amylic alcohol, 16¼ pts. sulphuric acid, and 16¼ pts. water, to flow slowly into a lukewarm solution of 12¼ pts. potassium-chromate, whereby sufficient heat is produced to cause the greater part of the valeral to distil over; towards the end, however, the distillation must be assisted by external heating. The oily layer of the distillate is separated, and shaken up, first with potash-ley, to remove valerianic acid formed at the same time, and then with acid sodium-sulphite, with which it forms a crystalline compound; the resulting crystals are pressed and washed with alcohol, and the valeral is separated therefrom by distillation with carbonate of sodium.

Properties.—Colourless, very mobile, strongly refracting liquid, neutral to vegetable colours, having a burning bitter taste, a pungent fruity odour, and exciting coughing when inhaled, like most compounds of the amyl-group. Specific gravity = 0·8057 at 17°, 0·8224 at 0° (Kopp). Boiling point 96° to 97° under the ordinary pressure, 92·8° under a pressure of 740 mm. (Kopp). After keeping for some time, the boiling-point rises, and a considerable portion of the valeral passes into a modification, probably polymeric, having a higher boiling-point. Valeral is very inflammable, and burns with a bright flame, exhibiting a faint blue colour on the edges.

Valeral is insoluble in *water*, but mixes in all proportions with *alcohol*, *ether*, and *volatile oils*. It dissolves *iodine*, *phosphorus*, and various *resins*, but not sulphur, and mixes with strong sulphuric acid.

Decompositions.—1. Valeral heated above its boiling point is transformed into an isomeric compound, boiling between 150° and 200°.—The same compound is found in the mother-liquor of the preparation of valeral-sodium-sulphite (p. 974), and is also formed by heating that salt with dry sodium-carbonate (Parkinson). According to Limpricht, on the other hand (Ann. Ch. Pharm. cxiv. 244), valeral is not converted into an isomer by heat, neither is any such body found in crude valeral.

2. Valeral exposed to the air is gradually converted into valerianic acid; the oxidation is accelerated by contact with platinum-black. The same change is produced by the action of a mixture of *potassium-chromate* and *sulphuric acid*, and by other oxidising agents.—*Nitric acid* of ordinary strength converts it into nitrovalerianic acid.—3. By the prolonged action of *chlorine*, valeral is converted into dichlorovaleral, which unites with acid ammonium-sulphite, forming the crystalline compound $C^5H^8Cl^2O.NaHSO^3$ (Kündig, Ann. Ch. cxiv. 1).—4. By distillation with *phosphoric pentachloride*, valeral is converted into the chloride $C^5H^{10}Cl^2$, which, when treated with alcoholic potash, gives up hydrochloric acid, and yields the compound C^5H^9Cl. (Ebersbach.)

5. The ammonia-compound of valeral is converted by *sulphydric acid* into valeraldine, a base homologous with thialdine (p. 772).

6. When valeral-ammonia is evaporated with *hydrocyanic acid*, the valeral is converted into leucine, just as aldehyde is converted into alanine (i. 63):

$$\underset{\text{Valeral.}}{C^5H^{10}O} + CNH + H^2O = \underset{\text{Leucine.}}{C^6H^{13}NO^2}.$$

7. With *cyanic acid*, valeral forms an acid, $C^7H^{13}N^3O^2$ (Baeyer), homologous with trigenic acid (p. 883):

$$C^5H^{10}O + 3CNHO = CO^2 + C^7H^{13}N^3O^2.$$

8. Valeral fused with *potassium-hydrate*, gives off hydrogen and yields valerate of potassium:

$$C^5H^{10}O + KHO = C^5H^9KO^2 + H^2.$$

9. When valeral is heated with *lime*, amylic alcohol and valerate of calcium are produced; and on distilling the mixture, decomposition-products of the latter are obtained, including the two compounds, $C^6H^{12}O$ and $C^7H^{14}O$, apparently consisting of mixed acetones—the former isomeric with caproic aldehyde, the latter with œnanthol. (Fittig, Ann. Ch. Pharm. cxvii. 68.)

10. When valeral is treated with *sodium*, ultimately with aid of heat, hydrogen is evolved, and a yellow sodium-compound is formed, which is decomposed by heating to 120° with ethylic iodide, yielding an oil, $C^9H^{18}O$, isomeric with valerone (Ebersbach). Borodin, on the other hand (Zeitschr. Ch. Pharm. 1864, p. 353; Jahresb. 1864, p. 337), obtained a mixture which was decomposed by water into caustic soda, valerate of sodium, amylic alcohol, and two new bodies, $C^{10}H^{22}O$ and $C^{10}H^{18}O$. The first of these is a monatomic alcohol, isomeric or identical with decatylic alcohol. It is a colourless aromatic oil, boiling at 203·3° and having a specific gravity of 0·8569 at 0°. It forms ethers with acetic and benzoic acids, reacts like other monatomic alcohols with pentachloride of phosphorus, forms a sulpho-acid when treated wlth oil of vitriol, and with sodium a compound analogous to sodium-ethylate. Its formation from valeral is represented by the equation:

$$\underset{\text{Valeral.}}{3C^5H^{10}O} + Na^2 = \underset{\substack{\text{Decatylate}\\\text{of sodium.}}}{C^{10}H^{21}NaO^2} + \underset{\substack{\text{Valerate}\\\text{of sodium.}}}{C^5H^9NaO}.$$

$$\underset{\substack{\text{Decatylate}\\\text{of sodium.}}}{C^{10}H^{21}NaO} + H^2O = NaHO + \underset{\substack{\text{Decatylic}\\\text{alcohol.}}}{C^{10}H^{22}O}.$$

The second body, $C^{10}H^{18}O$, isomeric with camphol, is a light-yellow, tasteless, neutral oil, insoluble in water, easily soluble in alcohol and ether, having a specific gravity of 0·9027 at 17°. Its boiling-point rises from 250° to 280° and 290°, without perceptible change of composition.

11. Valeral, treated for fifteen days with *sodium-amalgam* and water, is partly converted into amylic alcohol. (Wurtz, Ann. Ch. Pharm. cxxxiv. 201.)

12. Alsberg (Jahresb. 1864, p. 485), by heating a mixture of 1 vol. valeral, 3 vols. amylic alcohol, and 1 vol. acetic acid, obtained a compound, $C^5H^{10}(C^5H^{11})^2O^2$, which he calls diamylvaleral, but which has in reality the composition of the diamylic ether of amylene-glycol (p. 974). The same compound is produced, together with valerianic acid and a little amylic alcohol, by treating valeral with ethylate of sodium and absolute alcohol:

$$\underset{\text{Valeral.}}{5C^5H^{10}O} + \underset{\substack{\text{Sodium-}\\\text{ethylate.}}}{2C^2H^5NaO} + H^2O = \underset{\substack{\text{Sodium-}\\\text{valerate.}}}{2C^5H^9NaO^2} + \underset{\substack{\text{Diamylic}\\\text{amylenate.}}}{C^5H^{10}(C^5H^{11})^2O^2} + \underset{\substack{\text{Ethylic}\\\text{alcohol.}}}{2C^2H^6O}.$$

COMPOUNDS AND DERIVATIVES OF VALERAL.

Valeral-ammonia, $C^5H^{10}O.NH^3 = C^5H^9(NH^4)O$.—Valeral absorbs ammonia-gas, forming a thick syrup, which, after several weeks, deposits crystals of valeral-ammonia (Parkinson). According to Ebersbach, the compound is more easily prepared by adding aqueous ammonia to valeral mixed with a thousand times its bulk of water: the liquid immediately becomes milky, and after a few hours deposits crystals, the formation of which goes on for several months. Valeral-ammonia melts when heated, is insoluble in water, but dissolves easily in alcohol and ether. It is decomposed by sulphydric acid with formation of valeraldine, and by hydrocyanic acid with formation of leucine (p. 973).

Compounds of Valeral with Alkaline Bisulphites.—The *ammonium-salt*, $C^5H^9(NH^4)SO^3$, is deposited in shining laminæ on distilling a mixture of acid ammonium-sulphite and valeral, and leaving the distillate to evaporate. It is decomposed by water, acids, and alkalis, with separation of valeral.—The *sodium-salt*, $2C^5H^9NaSO^4.2H^2O$, is nearly insoluble in absolute alcohol and in ether, sparingly soluble in cold water; it dissolves without decomposition in water at 70° to 80°, but when more strongly heated with water, it is decomposed with separation of valeral and sulphurous acid. Alkalis and acids decompose it immediately. The air-dried crystals effloresce in a vacuum over oil of vitriol.

Compounds of Valeral with Acetic and Benzoic Anhydrides.—The compound $C^5H^{10}O.C^4H^6O^3$ is formed by heating 1 at. valeral with 1 at. acetic anhydride, or 2 at. acetic acid, to 200° in a sealed tube for four to eight hours, and passes over at 195° on submitting the oily product to fractional distillation. It is a colourless, ethereal, mobile, neutral liquid, of specific gravity 0·963, boiling at about 195°, insoluble in water, easily miscible with alcohol and ether. It is not altered by water, but in contact with potash is easily resolved into acetic acid and valeral (Kolbe and Guthrie, Ann. Ch. Pharm. cix. 296).—The *benzoic compound*, $C^5H^{10}O.C^7H^{10}O^3$, is obtained in like manner by heating valeral with benzoic anhydride to 260°, and passes over on rectification at 264°. It is a white crystalline body, tasteless and inodorous, insoluble in water, melting at 111°, and boiling at 264°. Alkalis decompose it into valeral and benzoic acid. (Kolbe and Guthrie.)

Dichlorovaleral, $C^5H^8Cl^2O$, is produced by the action of chlorine on valeral (p. 973)

Methylvaleral, $C^5H^9(CH^3)O$, is obtained by distilling a mixture of equivalent quantities of alkaline valerate and acetate, agitating the oily distillate with potash, and rectifying till the boiling-point becomes constant. It is an oily liquid boiling at 120°. (Williamson, Ann. Ch. Pharm. lxxxi. 86.)

Diamylvaleral (so-called), $C^{15}H^{32}O^2$.—This compound, isomeric or identical with diamylic amylenate, $\left.\begin{matrix}(C^5H^{10})''\\(C^5H^{11})^2\end{matrix}\right\}O^2$, the neutral amylic ether of amylenic glycol, is produced, as already observed (p. 973), by heating valeral with amylic alcohol and acetic acid, or with sodium-ethylate and absolute alcohol. It has a disagreeable odour like that of the amyl-compounds, and of celery, is insoluble in water, of specific gravity 0·849 at 7°, and boils at 255°.—*Diethylvaleral* (so-called), $C^5H^{10}(C^2H^5)^2O^2$, prepared by heating 1 vol. valeral with 4 vols. alcohol and 1 vol. acetic acid, is slightly soluble in water, has a pleasant fruity odour, a specific gravity of 0·835 at 12°, and boils at 158·2°.—*Dimethylvaleral* (so-called), $C^5H^{10}(CH^3)^2O^2$, prepared with 1 vol. valeral, 2·5 vols. methylic alcohol, and 0·5 vol. acetic acid, has an agreeable odour, a specific gravity of 0·852 at 10°, and boils at 124°. (Alsberg.)

VALERAL-AMMONIA. See preceding article.

VALERALDEHYDE.
VALERALDIDE. } Syn. with VALERAL.

VALERALDINE. $C^{15}H^{31}NS^2$. (Beissenhirtz, Ann. Ch. Pharm. xc. 109.—Parkinson, *ibid.* xc. 119.)—An organic base, homologous with thialdine, produced by the action of sulphydric acid on valeral-ammonia suspended in water. It is a viscid oil, which does not solidify at −20°, has a strong unpleasant odour, is insoluble in water, soluble in alcohol and ether, and volatilises without decomposition. It has an alkaline reaction, and unites with hydrochloric acid, forming the salt $C^{15}H^{31}NS^2.HCl$, which crystallises in needles, and when dissolved in water, yields with silver-nitrate, first chloride and then sulphide of silver.

VALERAMIC ACID. Syn. with AMIDOVALERIC ACID (p. 978).

VALERAMIDE. $C^5H^9O.H^2N$.—The primary amide of valeric acid, first prepared by Dumas, Malaguti, and Leblanc (Compt. rend. xxv. 475, 658), and further examined by Dessaignes and Chautard (Ann. Ch. Pharm. lxviii. 333). It is produced by the action of 7 or 8 vols. strong aqueous ammonia on 1 vol. ethylic valerate, and sublimes on evaporating the liquid in shining laminæ. It melts at 100°, and sublimes at a somewhat higher temperature. It is insoluble in water, gives off ammonia when boiled with alkalis, but is not decomposed thereby at ordinary temperatures; when heated with phosphoric anhydride, or passed in the state of vapour over red-hot lime, it is resolved into water and valeronitrile, or cyanide of tetryl, C^5H^9N (ii. 272). When ignited with potassium, it gives off hydrogen and carburetted hydrogen, and forms cyanide of potassium.

VALERAMINE. The name originally given by Wurtz to amylamine.

VALERANILIDE. $C^{11}H^{15}NO = C^5H^{10}(C^6H^5)NO^2$.—*Phenylvaleramide.*—Produced by the action of valeric anhydride on aniline. Crystallises in lustrous needles or prisms, sparingly soluble in water, easily in alcohol and ether. Melts at 115°, and distils, for the most part unaltered, at a temperature above 220°. It is but slowly attacked by caustic potash, and it is only by fusion with hydrate of potassium that any appreciable quantity of aniline can be obtained from it. (Chiozza, Ann. Ch. Phys. [3], xxxix. 201.)

VALERATES. See VALERIC ACID (p. 976).

VALERENE. Syn. with AMYLENE and with BORNEENE.

VALERIAN. The root of *Valeriana officinalis* contains starch, extractive matter, resin (about 6 per cent.), an essential oil, valeric acid, and the ordinary plant-constituents.

The essential oil of valerian is obtained by distillation with water, 1,000 pts. of the root yielding from 4 to 12 pts. of oil. It is a pale-yellow or greenish liquid, having a strong odour of valerian, an aromatic taste, and strong acid reaction. Specific gravity = 0·90 to 0·93°. Becomes viscid at −15°, but does not solidify completely even at −40°. Begins to boil at about 200°, the boiling-point gradually rising to above 400°.

Crude valerian-oil is a mixture of several substances. According to Pierlot (Ann. Ch. Phys. [3], lvi. 291), 100 pts. of it contain:

$$\begin{array}{l}25 \text{ pts. camphene, } C^{10}H^{16} \text{ (borneene, valerene).}\\ \;\;5 \text{ pts. valeric acid.}\\ \left.\begin{array}{l}18 \text{ pts. stearoptene}\\ 47 \text{ pts. resin}\\ \;\;5 \text{ pts. water}\end{array}\right\}\text{or 70 pts. valerol.}\end{array}$$

On submitting the crude oil to fractional distillation, a yellowish oil passes over between 120° and 200°, containing nearly all the valeric acid and the borneene (i. 626); afterwards, according to Gerhardt (Ann. Ch. Phys. [3], vii. 275), an oxygenated oil, valerol; according to Pierlot, this oil may be resolved, by further fractional precipitation, and distillation over potassium-hydrate, into a camphor or stearoptene, a resin, valeric acid, and water.

VALERIANIC or **VALERIC ACID.** $C^5H^{10}O^2 = \left.\begin{array}{c}C^5H^9O\\H\end{array}\right\}O$.—*Delphinic Acid. Phocenic Acid. Butylcarbonic Acid. Baldriansäure.* (Chevreul [1817], *Recherches sur les corps gras*, pp. 99, 209.—Grote, Brandes' Arch. xxxiii. 160.—Trommsdorff and Ettling, Ann. Ch. Pharm. vi. 176.—Dumas and Stas, *ibid.* xxxv. 145.—Balard, *ibid.* lii. 311.—Meyer and Zenner, *ibid.* lv. 317.—Moro, *ibid.* lv. 330.—Redtenbacher, *ibid.* lix. 41.—Hlasiwetz, *ibid.* lxxi. 40.—Winckler, Repert. Pharm. xxvii. 169.—Krämer, Brandes' Arch. xl. 269; xliii. 21.—P. Morin. J. Pharm. [3], vii. 299.)—This acid, related to amylic alcohol in the same manner as acetic acid to ethylic alcohol, was first obtained by Chevreul, in 1817, from the fat of *Delphinum Phocæna*, and thence called delphinic or phocenic acid. Grote, in 1830, obtained from essential oil of valerian an acid which he designated as valerianic acid. This was shown by Trommsdorff and Ettling to be identical with Chevreul's phocenic acid, and the same acid was afterwards produced by oxidation of amylic alcohol, by Dumas and Stas, who established its composition and its relation to amylic alcohol.

Valeric acid appears to be somewhat widely diffused in the vegetable kingdom, being found in valerian-root, angelica-root, the root of *Athamanta oreoselinum*, the fruit and bark of the guelder rose (*Viburnum Opulus*), the bark of the elder-tree, and in many plants of the composite order. It is also found in many animal oils and other animal secretions. It is a frequent product of the oxidation of fats and of the putrefaction of albuminous substances, &c. Amylic alcohol yields, by oxidation, valerianic acid, together with valeral and amylic valerate.

Preparation.—By oxidation of amylic alcohol.—A mixture of 1 pt. amylic alcohol and 2 pts. strong sulphuric acid is allowed to flow slowly into a solution of 5 pts. acid potassium-chromate in water; and when the first action, which takes place spontaneously, is over, the mixture is heated for some time in a flask provided with a vertical condensing-tube, in order to convert the valeral produced in the first instance into valeric acid.

The liquid is then distilled; the distillate saturated with carbonate of sodium; the amylic valerate contained in it is distilled off; and the dry residue of sodium-valerate is dissolved in an equal weight of water and distilled with sulphuric acid ($\frac{1}{2}$ to $\frac{3}{5}$ pt. oil of vitriol to 1 pt. sodium-salt). The distillate consists of an aqueous solution of valeric acid, surmounted by an oily layer consisting of a definite hydrate, $C^5H^{10}O^2.H^2O$, from which the pure acid or hydric valerate, $C^5H^{10}O^2$, may be obtained by rectification, a milky aqueous distillate passing over at first, and afterwards, at 175°, the pure acid, in the form of a clear oily liquid.

Properties.—Pure valeric acid, or hydric valerate, is a colourless mobile oil, having a sour burning taste, and a strong peculiar odour, like that of valerian-oil, somewhat also like that of butyric acid and decayed cheese. Specific gravity = 0·937 at 16° (Dumas and Stas); 0·9378 at 19·6°, and 0·9555 at 0° (Kopp); 0·9558 at 15° (Mendelejef). Index of refraction, 1·3952 (Delffs). It is active or inactive to polarised light, according as it has been prepared from active or inactive amylic alcohol: the active modification produces a rotation of 17° to the left in a tube 50 centimetres long (Pedler, Chem. Soc. J. xxi. 74). It remains liquid and transparent at −15°, makes transient grease-spots on paper, boils at 175° (Dumas and Stas; Persin): at 175·8° under a pressure of 746 mm. (Kopp). The specific gravity of its vapour, when determined at a sufficiently high temperature, is 3·66; calc. for 2 vols. = 3·53.

Hydric valerate, ($C^5H^{10}O^2$), dissolves in 30 pts. water at 12°, mixes in all proportions with alcohol and ether, and dissolves abundantly in strong acetic acid. It dissolves water, and forms an oily hydrate, $C^5H^{10}O^2.H^2O$ (commonly called the trihydrate, from having been regarded as $C^{10}H^{18}O^3.3H^2O$), which separates on decomposing a valerate with sulphuric acid not too much diluted; or on adding chloride of calcium, or other dehydrating salt, or phosphoric anhydride, to an aqueous solution of the acid. This hydrate is oily, like the pure hydric valerate, but has a higher specific gravity (0·950, according to Trautwein), and a lower boiling-point; when it is heated, aqueous valeric acid first passes over, and afterwards pure hydric valerate.

Valeric acid mixes with oil of turpentine, and dissolves phosphorus, camphor, and some resins.

Decompositions.—1. Valeric acid vapour passed through a red-hot tube, is resolved into carbonic oxide, carbonic anhydride, and a mixture of hydrocarbons of the olefine group (ethylene, tritylene, and tetrylene), sometimes also mixed with marsh-gas (Hofmann, Chem. Soc. Qu. J. iii. 121).—2. When an *electric current* is passed through a solution of potassic valerate, the valeric acid is resolved, with absorption of oxygen into tetryl and carbonic anhydride:

$$\underset{\substack{\text{Valeric}\\\text{acid.}}}{2C^5H^{10}O^2} + O = \underset{\text{Tetryl.}}{C^8H^{18}} + 2CO^2 + H^2O.$$

The tetryl is, however, converted by further oxidation into tetrylene and water:

$$C^8H^{18} + O = 2C^4H^8 + H^2O;$$

or it is oxidised to tetrylic oxide, $(C^4H^9)^2O$, which then reacts with the valeric acid to form tetrylic valerate (Kolbe, Ann. Ch. Pharm. lxix. 257).—3. By *potassic permanganate* in alkaline solution, valeric acid is oxidised to carbonic acid, oxalic acid, butyric acid, and its lower homologues, together with a volatile solid acid, perhaps angelic acid (Neubauer, Ann. Ch. Pharm. cvi. 59).—4. Valeric acid dissolves, with evolution of heat, in strong *sulphuric acid*, apparently forming a conjugated acid.—5. Strong *nitric acid* slowly converts it into nitrovaleric acid.—6. With *chlorine* and *bromine* it also forms substitution-products. It dissolves *iodine*, but without forming an iodated acid.—7. With *pentachloride* or *oxychloride of phosphorus*, it forms valeric chloride or valeric anhydride.—8. When heated with *pentasulphide of phosphorus*, it forms thiovaleric acid, a liquid having an extremely offensive odour, and probably consisting of $C^5H^{10}OS$. (Ulrich, Ann. Ch. Pharm. cx. 281.)

Valerates.—Valeric acid is monobasic, forming neutral salts, $C^5H^9MO^2$, and a few acid and basic salts. The valerates are produced by direct saturation. They are unctuous to the touch, inodorous when dry, but smell of valeric acid when moist, especially if they are also warmed; they have a sweetish taste, with somewhat pungent after-taste. Most of them dissolve in water, a few also in alcohol; many of them rotate on the water in the act of dissolving. By dry distillation, they yield chiefly valerene and valerone. A mixture of valerate and formate subject to dry distillation yields valeral; a mixture of valerate and acetate yields, in like manner, methylvaleral (p. 975). The soluble valerates are decomposed by the electric current, with formation of carbonic acid, tetrylene, and tetrylic valerate.

Valerates are decomposed by mineral acids and by many organic acids: *e.g.* acetic, tartaric, citric, malic acid, &c., with separation of valeric acid. Butyric acid does not decompose them; on the other hand, butyrates heated with valeric acid yield free butyric acid. On this reaction is founded a method of separating butyric and valeric acids, by partial saturation with potash, whereby only valerate of potassium is at first produced. When a mixture of acetic and valeric acids is partially neutralised with potash, and heated, acid acetate of potassium remains behind. (Liebig, see ANALYSIS, i. 250.) Valeric acid is further distinguished from butyric acid, which it resembles in many respects, by the behaviour of its cupric salt (*infra*).

Valerate of Ammonium, $C^5H^9(NH^4)O^2$, easily gives off ammonia when heated. It dissolves freely in water and in alcohol. When heated with phosphoric anhydride, it yields valeronitrile. This salt is formed in the putrefaction of organic bodies, and is a frequent constituent of mouldy cheese.—The *potassium-salt*, $C^5H^9KO^2$, solidifies on evaporation, to an amorphous, white, deliquescent, saline mass, having an alkaline reaction, very soluble in water and in strong alcohol, soluble in less than 3·9 pts. of absolute alcohol at 20°. It melts at 140°, and decomposes at a stronger heat. When distilled with arsenic, it yields a heavy, oily, alliaceous, fuming liquid, probably the cacodyl of valeric acid (Gibbs, Sill. Am. J. [2], xv. 118).—The *sodium-salt* crystallises, by spontaneous evaporation in dry air at 32°, in cauliflower-like masses, extremely deliquescent, very soluble in water, and even in absolute alcohol, melting at 140°.—The *lithium-salt*, $2C^5H^9LiO^2.H^2O$, crystallises from the syrupy solution, in spherical warty masses.

Valerate of Barium, $C^{10}H^{18}Ba''O^4.2H^2O$, crystallises by spontaneous evaporation in shining, easily friable crystals, which dissolve in 2 pts. water at 15°, in 1 pt. at 20°, exhibiting a very brisk rotation, and are sparingly soluble in alcohol. They give off from 2 to 2½ per cent. water on exposure to the air at 25°, the rest (about 7 per cent.) when heated; the dry salt decomposes at a dull red heat, giving off an inflammable gas, probably tetrylene, yielding a strong-smelling distillate of valeral, with a little valerone, and leaving carbonate of barium mixed with a little charcoal.—The *calcium-salt*, $C^{10}H^{18}Ca''O^4.H^2O$, crystallises by slow evaporation in stellate groups of prisms and needles, easily soluble in water and in ordinary alcohol, sparingly soluble in absolute alcohol, melting with decomposition at 150°. A mixture of 6 pts. valerate of calcium and 1 pt. lime yields, by dry distillation, a mixture of valerone and valeral.—The *strontium-salt* crystallises in four-sided tables.—The *magnesium-salt* is obtained, by slow evaporation, in tufts of transparent prisms, moderately soluble in water, slightly soluble in alcohol.

The *cupric salt* separates from the blue-green solution of cupric carbonate in the aqueous acid, in green monoclinic prisms containing $C^{10}H^{18}Cu''O^4.H^2O$, soluble in water and in alcohol. When concentrated valeric acid is added to a solution of cupric acetate, and the liquid agitated, anhydrous cupric valerate separates after a while in oily drops, which in five to twenty minutes change into a greenish-blue crystalline powder of the hydrated salt. According to Larocque and Huraut (J. Pharm. [3] ix. 430), this reaction distinguishes valeric from butyric acid, which, when added to cupric acetate, immediately forms a crystalline precipitate.

Iron-salts.—*Neutral ferric valerate* has not been obtained in the separate state. Valerate of sodium added to ferric chloride, throws down a mixture of neutral and basic salt, which, after drying, forms a dark brick-red, amorphous powder. Iron dissolves in aqueous valeric acid with evolution of hydrogen, forming *ferrous valerate.*

Lead-salts.—The *neutral salt*, $C^{10}H^{18}Pb''O^4$, separates from solution by slow evaporation, in shining, easily fusible laminæ.—A *basic salt*, $C^{10}H^{18}Pb''O^4.2PbO$, is obtained, by treating valeric acid with excess of litharge, exhausting with cold water, and evaporating the filtrate in a vacuum over oil of vitriol, in hemispherical groups of shining needles, infusible and sparingly soluble in water.

Mercury-salts.—The *neutral mercuric salt* separates, on mixing mercuric chloride with valerate of sodium, in slender white needles, which are also deposited on boiling the basic salt with water, and leaving the filtrate to cool. The basic salt, which has a red colour, is obtained by moderately heating the neutral salt, or by dissolving mercuric oxide in warm concentrated valeric acid. It is insoluble in cold water, and is decomposed by boiling water into the neutral salt and a red residue.—The *mercurous salt* separates in small needles from a solution of mercurous oxide in hot concentrated valeric acid.

The *silver-salt*, $C^5H^9AgO^2$, separates on evaporation, in white shining laminæ. On adding an alkaline valerate to nitrate of silver, a curdy precipitate is formed which gradually becomes crystalline. The salt blackens on exposure to light, and is decomposed by heat.

Zinc-salt, $C^{10}H^{18}Zn''O^4$.—Metallic zinc dissolves slowly in aqueous valeric acid. The aqueous acid saturated by boiling with zinc-carbonate and filtered hot, deposits the anhydrous zinc-salt in nacreous scales resembling boric acid. The same salt is obtained by precipitation. According to Duclou, it dissolves in 50 pts. cold and 40 pts. boiling water, in 17·5 pts. cold and 16·7 pts. boiling alcohol; according to Wittstein, it dissolves in 90 pts. cold water, in 60 pts. cold alcohol of 80 per cent., in 500 pts. cold and 200 pts. boiling ether. The aqueous solution gives off valeric acid on boiling. The salt melts at 140°, and decomposes at a higher temperature.—A *hydrated salt*, $C^{10}H^{18}Zn''O^4.12H^2O$, is obtained by mixing equivalent quantities of hydric valerate and recently precipitated zinc-carbonate with a small quantity of water, and drying at a gentle heat. It does not differ in appearance from the anhydrous salt, gives off all its crystallisation-water at 100°, and dissolves in 44 pts. of cold water, the solution, when evaporated, yielding crystals of the anhydrous salt (Wittstein). Valerate of zinc is used as a remedy in nervous disorders. The commercial salt is said to be sometimes contaminated with butyrate, the presence of which may be detected by separating the acid, and testing with acetate of copper in the manner already described (p. 977).

Substitution-derivatives of Valeric Acid.

Amidovaleric Acid, $C^5H^{11}NO^2 = C^5H^9(NH^2)O^2$. *Valeramic Acid. Valeramidic Acid.*—This acid, which might also be regarded as *oxyvaleramic acid*, $\left.\begin{matrix}H^2\\(C^5H^8O)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$, was found by Gorup-Besanez (Ann. Ch. Pharm. xcviii. 15), together with leucine (amidocapric acid) in the pancreas of an ox. It is produced artificially by the action of ammonia on an alcoholic solution of bromovaleric acid:

$$C^5H^9BrO^2 + 2NH^3 = C^5H^{11}NO^2 + NH^4Br.$$

(Cahours, Ann. Ch. Pharm. Suppl. ii. 83.—Fittig and Clark, Zeitschr. f. Chem. 1865, p. 503). It might probably also be formed, similarly to the homologous amic acids, by reducing nitrovaleric acid with sulphydric acid, and by the action of hydrocyanic and hydrochloric acids on butyral.

Amidovaleric acid was prepared from the pancreas of the ox by extraction with cold water. The solution was boiled, the filtrate mixed with excess of baryta-water to separate phosphoric acid, and the filtrate evaporated to a syrup over the water-bath; whereupon it deposited a mixture of leucine and amidovaleric acid, which were separated by fractional solution in alcohol of specific gravity 0·82, the amidovaleric acid being much less soluble than the leucine. It was ultimately purified by recrystallisation from strong alcohol.

Amidovaleric acid closely resembles leucine (amidocapric acid), but is less soluble in water and in alcohol, especially in the latter; it is insoluble in ether. It unites with acids, forming crystallisable compounds, which are much more soluble than the corresponding leucine-salts. It dissolves easily, and without decomposition, in aqueous alkalis, forming, for the most part, crystallisable compounds.

When heated in a glass tube, it melts and sublimes, with partial decomposition, giving off alkaline vapours having a strong odour of herring-pickle, probably tetrylamine. When heated in the air, it burns quickly with a bluish flame.

Bromovaleric Acid, $C^5H^9BrO^2$.—Produced by the action of bromine on valeric acid at 140°—150° (Cahours, Ann. Ch. Pharm. Suppl. ii. 74), or on valerate of silver (Borodine, *ibid.* cxix. 121). It is a colourless heavy oil, having a pungent odour, and boiling, according to Cahours, between 226° and 230°, without perceptible decomposition; according to Borodine, on the other hand, it is decomposed by boiling, giving off hydrobromic acid, yielding a distillate containing valeric acid, and apparently valeral, and leaving a carbonaceous residue.

Bromovaleric acid separates valeric acid from valerates. Its compounds with the alkalis and alkaline earths are easily soluble and not crystallisable. The silver-salt is white, insoluble, and very unstable. (Borodine.)

This acid is easily etherified; its ethylic ether boils between 190° and 194°.

Chlorovaleric Acids. *Trichlorovaleric* or *Chlorovalerisic acid*, $C^5H^7Cl^3O^2$, is formed by passing chlorine-gas into hydric valerate in the dark, the liquid being cooled at first, and afterwards warmed to 50° or 60°; the excess of chlorine is expelled by a stream of carbonic anhydride. Trichlorovaleric acid is an oily liquid, very viscid at $-18°$; not very mobile at ordinary temperatures, but perfectly mobile at 30°. It is inodorous, has a sharp burning taste, is heavier than water, and decomposes at 110°—120°, with evolution of hydrochloric acid. In contact with water it forms a very fluid hydrate, which sinks to the bottom of the water. The acid dissolves in aqueous alkalis, but is precipitated therefrom by acids in its original state. The aqueous solution forms, with nitrate of silver, a precipitate soluble in nitric acid. (Dumas and Stas.)

Tetrachlorovaleric or *Chlorovalerosic acid*, $C^5H^6Cl^4O^2$, is formed by the prolonged action of an excess of chlorine on valeric acid in sunshine, the action being ultimately assisted by heating the liquid to 60°. It is a colourless, inodorous, semifluid oil, having a sharp, burning, bitter taste, heavier than water, not solidifying at $-15°$, not volatile, decomposing when heated above 150°. It unites with water, forming an oily hydrate,

$C^5H^6Cl^4O^2.H^2O$, and dissolves in a large quantity of water, easily also in alcohol and ether. The solutions, after a while, contain free hydrochloric acid. The acid is easily decomposed by fixed alkalis, but not by ammonia.

Tetrachlorovaleric acid decomposes carbonates. The alkaline tetrachlorovalerates are easily soluble in water; the rest insoluble or sparingly soluble.—The *silver-salt*, $C^5H^5AgCl^4O^2$, obtained by precipitation from the ammonium-salt, is white, slightly soluble in water, easily in nitric acid; the solution, when exposed to light, deposits chloride of silver. The dry salt decomposes slowly in the dark, forming chloride of silver, and a substance which makes grease-spots on paper—probably trichloroxyvaleric acid, $C^5H^7Cl^3O^3$. (Dumas and Stas.)

Nitrovaleric Acid, $C^5H^9(NO^2)O^2$. (Dessaignes, Ann. Ch. Pharm. lxix. 274.) —Formed by the action of strong nitric acid at the boiling heat on valeric acid; crystallises from the acid solution in thin needles, from water in rhombic plates. It sublimes at 100°, but its boiling-point is much higher.—*Nitrovalerate of lead* is easily soluble, and crystallises in thin prisms.—The *ferric salt* is insoluble, and resembles ferric succinate.—The *barium-* and *calcium-salts* are very soluble, the latter crystallising in needles.—The *silver-salt*, $C^5H^8Ag(NO^2)O^2$, crystallises from boiling water in slender prisms.

Dessaignes is of opinion that the acid designated as nitrovaleric acid may perhaps be nitro-angelic acid, $C^5H^7(NO^2)O^2$.

VALERIAN-OIL. See VALERIAN (p. 975).

VALERIC ALDEHYDE. Syn. with VALERAL (p. 973).

VALERIC ANHYDRIDE. $C^{10}H^{18}O^3 = (C^5H^9O)^2O$. *Valeric Oxide. Valeric Valerate. Anhydrous Valeric Acid.* (Chiozza, Ann. Ch. Pharm. lxxxiv. 106.) —Prepared by decomposing 6 at. dry valerate of potassium with rather more than 1 at. oxychloride of phosphorus, and purified by washing the distillate with carbonate of sodium, dissolving it in ether, and evaporating. It is a colourless, moderately mobile oil, not miscible with water. When recently prepared it has a faint and not unpleasant odour of apples, but when rubbed between the fingers, it emits the offensive odour of valeric acid. Specific gravity = 0·934 at 15°. Boiling-point, 215°. Vapour-density = 6·23. It slowly absorbs *water*, and is converted into valeric acid. When heated with an *alkali*, it is instantly converted into a valerate. On gently warming it with a small quantity of *potassic hydrate*, a violent action takes place, and free valeric acid is formed as well as potassic valerate:

$$(C^5H^9O)^2O + KHO = C^5H^9O.K.O + C^5H^9O.H.O.$$

With *alcohol* it quickly forms ethylic valerate; hence the ether used in purifying it must be free from alcohol.—By *ammonia* it is quickly converted into valeramide; by *aniline* into valeranilide.

Benzovaleric anhydride, $C^7H^5O.C^5H^9O.O$, is produced by the action of benzoic chloride on potassic valerate (i. 558), and other double anhydrides containing valeryl may be formed in a similar manner.

VALERIC BROMIDE, C^5H^9OBr, is produced by the action of phosphoric pentabromide on valeric acid. It is a liquid boiling at 143°. (Béchamp.)

VALERIC CHLORIDE, C^5H^9OCl, is produced by the action of phosphoric oxychloride on valerate of sodium (Moldenhauer), or of phosphorous chloride on valeric acid (Béchamp). It is a colourless, mobile, fuming liquid, having a specific gravity of 1·005 at 6°, and boiling between 115° and 120°; easily decomposed by water into hydrochloric and valeric acid. (Béchamp, Compt. rend. xlii. 224.—Moldenhauer, Ann. Ch. Pharm. civ. 111.)

VALERIC ETHERS. The valerates of methyl, ethyl, and amyl are prepared by distilling valerate of sodium with sulphuric acid and the corresponding alcohols.

Methylic Valerate, $C^5H^9(CH^3)O^2$, is a colourless liquid, having an odour like that of wood-spirit and valerian together. Specific gravity = 0·8869 at 15°; 0·9015 at 0°. Boils at 116°. Specific heat (between 45° and 21°) = 0·491. (Kopp.)

Ethylic Valerate, $C^5H^9(C^2H^5)O$, is a colourless liquid, having a fruity odour, also like that of valerian. Specific gravity = 0·866 at 18° (Kopp), 0·894 at 0° (Otto). Index of refraction = 1·3904 (Delffs). Boils at 133° (Otto; Kopp; Berthelot); at 131° (Delffs). Dissolves sparingly in water, easily in alcohol. Ammonia converts it into valeramide.

Ethylic valerate dissolves sodium, with little or no evolution of hydrogen. Wanklyn (Chem. Soc. J. xvii. 371), by heating 2 grms. sodium with 6 grms. ethylic valerate and 7·5 grms. pure ether, obtained an oily body, having approximately the composition of valeryl:

$$\underset{\text{Ethylic valerate.}}{2(C^5H^9O.C^2H^5.O)} + Na^2 = \underset{\text{Sodium-ethylate.}}{2C^2H^5NaO} + \underset{\text{Valeryl.}}{(C^5H^9O)^2}.$$

Geuther and Greiner (Jahresb. 1865, p. 319) obtained no valeryl, but the sodium-salt of a crystallisable acid, and an oily body, which, when distilled, yielded, as principal product, a liquid boiling, like the so-called diamylvaleral (p. 974), between 240° and 260°.

Amylic Valerate, $C^5H^9(C^5H^{11})O$, is prepared as above, and is likewise formed in the preparation of valeric acid by oxidising amylic alcohol with sulphuric acid and potassic chromate, being contained in the oily liquid separated from the valerate of sodium (p. 975). It is an oily liquid, having an agreeable fruity odour. Specific gravity = 0·8645 at 17°. Boiling-point 187° to 188° (Kopp); 196° (Balard). Vapour-density = 6·1. A solution of this ether in 6 to 8 pts. alcohol has a strong odour of apples, and is used for aromatising sugar, &c.

Cetylic Valerate, $C^5H^9(C^{16}H^{33})O$, has a specific gravity of 0·852 at 20°, melts at 25°, solidifies again at 20°, and boils at 280°—290°. (E. Dollfus, Ann. Ch. Pharm. cxxxi. 283.)

VALERIC IODIDE, C^5H^9OI, is prepared by distilling an anhydrous valerate with iodide of phosphorus, and rectifying the distillate over mercury. It is a heavy nearly colourless liquid, boiling at 108°, quickly decomposed by water and by alcohol. (Cahours, Compt. rend. xliv. 1252.)

VALERIC OXIDES. The *protoxide*, $(C^5H^9O)^2O$, has been already described as valeric anhydride (p. 979).

Valeric Peroxide, $C^{10}H^{18}O^4 = (C^5H^9O)^2O^2$, is produced by the action of hydrated barium-peroxide on valeric anhydride. It is a heavy oily liquid, slightly soluble in water, exploding slightly when heated, and acting as an oxidising agent when suspended in water. (Brodie, Proc. Roy. Soc. xii. 655.)

VALERINS. Glycerides produced by heating valeric acid with glycerin. The delphinin or phocenin which Chevreul obtained by treating dolphin-oil with alcohol, was probably a mixture of trivalerin with monovalerin and divalerin.

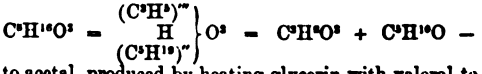
Monovalerin, $C^8H^{16}O^4 = (C^3H^5)'''(HO)^2.(C^5H^9O^2) = C^5H^{10}O^2 + C^3H^8O^3 - H^2O$. —Produced by heating valeric acid with excess of glycerin to 200° for three hours, and purified with potash-ley, &c. in the usual way. It is also formed by the action of hydrochloric acid gas on a mixture of glycerin and valeric acid. Oily neutral liquid having a faint odour, and a specific gravity of 1·100 at 16°. Mixes with half its bulk of water to a clear liquid; separates, on addition of more water, and mixes with 100 vols. water to a liquid having the character of an emulsion. By contact with the air for some weeks it becomes acid, and then contains free valeric acid, but the alteration is not attended with any perceptible absorption of oxygen. Alcohol and hydrochloric acid decompose it, even in the cold, forming ethylic valerate and glycerin. Aqueous ammonia slowly converts it into valeramide.

Divalerin, $C^{13}H^{24}O^5 = (C^3H^5)'''.HO.(C^5H^9O^2)^2 = C^3H^8O^3 + 2C^5H^{10}O^2 - 2H^2O$. —Produced by heating glycerin with valeric acid to 275°. Oily liquid, having a disagreeable fishy odour and a bitter aromatic taste. Specific gravity = 1·059 at 16°. Solidifies at −40°, but remains soft and transparent; does not mix readily with water. Its reactions are similar to those of monovalerin.

Trivalerin, $C^{18}H^{32}O^6 = (C^3H^5)'''(C^5H^9O^2)^3 = C^3H^8O^3 + 3C^5H^{10}O^2 - 3H^2O$. —Produced by heating divalerin to 220° with 8 or 10 times its weight of valeric acid. It is a neutral oily liquid, having a faint unpleasant odour, insoluble in water, but soluble in alcohol and ether; decomposed by alcohol and hydrochloric acid like the other valerins. (Berthelot.)

VALERISIC ACIDS, in the nomenclature of Laurent and others, are substitution-products of valeric acid, in which 3 at. hydrogen are replaced by chlorine or other radicles, *e.g.* chlorovalerisic acid, $C^5H^7Cl^3O^2$. In like manner, those products in which 4 at. hydrogen are thus replaced, are called valerosic acids.

VALERODICHLORHYDRIN, $(C^3H^5)'''(C^5H^9O)OCl^2$, is produced by heating epichlorhydrin (i. 894) with chloride of valeryl to 100°. It is a mobile liquid, smelling like amylic acetate, having a specific gravity of 1·149 at 11°, and boiling at 245°, under a pressure of 737 mm. (Truchot, Ann. Ch. Pharm. cxxxviii. 297.)



VALEROGLYCERAL. $C^8H^{16}O^3 = \left.\begin{matrix}(C^3H^5)''' \\ H \\ (C^5H^{10})''\end{matrix}\right\} O^3 = C^3H^8O^3 + C^5H^{10}O - H^2O$.—A compound analogous to acetal, produced by heating glycerin with valeral to 170°—180° for 24 hours. It is a liquid boiling between 224° and 228°. Specific gravity = 1·027 at 0°. Vapour-density, obs. = 5·526; calc. = 5·544. It is insoluble in water, has only a faint odour, but is decomposed by moist air, and then emits an odour like that of valeral. (Harnitz-Harnitzky and Menschutkin, Ann. Ch. Pharm. cxxxvi. 126; Jahresb. 1865, p. 506.)

Similar compounds are obtained with acetic and benzoic aldehydes.

VALEROL. $C^6H^{10}O$?—The neutral oxygenated constituent of valerian-oil p. 975). It was first prepared and examined by Gerhardt (Ann. Ch. Phys. [3], vii. 275), and afterwards found by Personne (Compt. rend. xxxvii. 309) in the volatile oil of lupulin. It is prepared by rapidly distilling valerian-oil in a stream of carbonic anhydride, whereupon borneene (valerene), borneol, and valeric acid pass over first, and afterwards valerol. The latter is heated to 200°, for some time, in an atmosphere of carbonic anhydride, then cooled in ice, and the valerol which crystallises out is washed with aqueous sodic carbonate, rectified several times in carbonic anhydride, and crystallised by cooling (Gerhardt). According to Pierlot (Ann. Ch. Phys. [3], lvi. 294), it must be distilled over hydrate of potassium, to free it completely from valeric acid.

Valerol crystallises at 0° in colourless transparent prisms. It melts at 20°, then remains liquid at ordinary temperatures, and does not solidify till cooled to 0°. In the liquid state it floats on water. It is slightly soluble in water, easily soluble in alcohol, ether, and volatile oils. According to Pierlot, its boiling-point is not constant, but varies during distillation from 200° to 430° without remaining stationary at any intermediate point; in fact, valerol is not a definite compound, but a mixture of the stearoptene of valerian-oil (p. 975), with resin and a little water. According to Gerhardt and Cahours, it is converted into valeric acid by atmospheric oxidation, and when heated with potassic hydrate gives off hydrogen, and yields valerate and carbonate of potassium:

$$C^6H^{10}O + 3KHO + H^2O = C^5H^9KO^2 + K^2CO^3 + 3H^2.$$

According to Pierlot, on the other hand, it is not converted into valeric acid by exposure to the air, or by treatment with any oxidising agent, and if quite free from valeric acid is not acted upon by potash.

VALEROLACTIC ACID. $C^5H^{10}O^3$.—Syn. with ethyl-lactic acid (see Lactic Ethers, iii. 463). According to J. Clark (Jahresb. 1865, p. 319), it is produced by heating bromovaleric acid with silver-oxide and water. Its zinc-salt crystallises readily.

VALERONE. $C^9H^{18}O = \left.\begin{matrix}C^5H^9O\\C^4H^9\end{matrix}\right\} = \left.\begin{matrix}C^5H^9\\C^4H^9\end{matrix}\right\}O$.—*Valeryl-butyl. Valene. Valeroyl-butyloxide. Dibutylacetone. Dibutylcarbonoxyd.*—This body, the ketone of valeric acid, is produced by the distillation of valerates, the calcium-salt being generally used. It was first prepared by Löwig (Pogg. Ann. xlii. 412), mixed, however, with a large quantity of valeral; pure valerone was first obtained by Ebersbach (Ann. Ch. Pharm. cvi. 268), who separated the valeral by means of acid sulphite of sodium. The best mode of preparing it is to distil valerate of calcium with one-sixth of its weight of lime; the quantity obtained, however, is but small, probably because the greater part of it is resolved into valeral and tetrylene: $C^9H^{18}O = C^5H^{10}O + C^4H^8$. Valerone is a transparent, colourless, mobile liquid, having a pleasant ethereal odour and burning taste. It is lighter than water, does not mix with it, but dissolves in alcohol and ether. It boils at 165°, does not combine with acid sulphite of sodium, and is decomposed by sodium and by pentachloride of phosphorus only when heated.

VALERONITRILE. C^5H^9N.—Syn. with Cyanide of Tetryl, $C^4H^9.CN$. (See Cyanides, ii. 272.)

VALERONYL. Löwig's name for the hydrocarbon C^4H^9

VALEROSIC ACIDS. See Valerisic Acids (p. 980).

VALEROXYL. Syn. with Valeryl.

VALEROYL. A name applied to the hydrocarbon C^5H^9, according to which denomination, valerene or amylene may be designated as hydride of valeroyl, $C^5H^9.H$, &c., valerone as valeroyl-butyloxide, $C^5H^9.C^4H^9.O$, &c.

VALERUREID. Syn. with Valerylurea. (See Carbamides, i. 753.)

VALERYL. C^5H^9O. *Valeroxyl.*—The radicle of valeric acid and its derivatives. According to Wanklyn, it is obtained in the free state by the action of sodium on ethylic valerate (p. 979).

The bromide, chloride, &c. of valeryl are described as valeric bromide, &c. (p. 979); the protoxide as valeric anhydride (p. 979); the peroxide as valeric peroxide (p. 980).

VALERYLAMIDIC ACID. Syn. with Amidovaleric Acid (p. 978).

VALERYL-BUTYL. Syn. with Valerone.

VALERYLENE. C^5H^8. (Reboul, Ann. Ch. Pharm. cxxxi. 238; cxxxii. 117; cxxxv. 372; Jahresb. 1864, p. 505; 1865, p. 509.)—This hydrocarbon, homologous with acetylene, is obtained by heating bromide of amylene with concentrated alcoholic potash to 140° for several hours, distilling the liquid separated from the product by water, and collecting that which passes over from 44° to 46°. It is a colourless very mobile liquid, which floats on water, and is nearly insoluble therein. It has a pungent alliaceous odour, boils at 44° to 46° under a pressure of 745 mm., has a vapour-density of 2·356 (calc. 2·354). It is not absorbed by an ammoniacal solution of cuprous chloride.

Bromine-compounds of Valerylene.—Valerylene shaken up with strong aqueous hydrobromic acid, becomes hot and is converted into a red oil, which, after washing with alkaline water, yields, by fractional distillation, the two following compounds:

Monohydrobromate of valerylene, $C^5H^8.HBr$, boiling at 112°;
Dihydrobromate of valerylene, $C^5H^8.2HBr$, „ 170°—175°.

The former, which is the chief product, is distinguished from the isomeric body monobromamylene, C^5H^9Br, boiling at 115°, chiefly by its property of forming with bromine a liquid compound, $C^5H^8.HBr.Br^2$, whereas monobromamylene forms with bromine a crystallisable compound, $C^5H^9Br.Br^2$.

When bromine is added by drops to valerylene cooled by a freezing mixture, a fresh quantity of valerylene added before the red colour appears, then more bromine, and so on alternately, a heavy oil is formed containing two liquid bromine-compounds, $C^5H^8Br^2$ and $C^5H^8Br^4$, in various proportions. If the addition of bromine be discontinued when no more instantaneous decoloration takes place, the product consists mainly of the dibromide; in the contrary case, provided the action be sufficiently prolonged, nothing but tetrabromide is obtained. In sunshine the tetrabromide forms in an hour or two, together with the crystalline compound, $C^5H^7Br.Br^4$ (*a*).

Tetrabromide of Valerylene, $C^5H^8Br^4$, is a thick very heavy liquid, which does not solidify at −10°; it is isomeric with the (probably solid) bromide of dibromamylene, $C^5H^8Br^2.Br^2$.

Dibromide of Valerylene, $C^5H^8Br^2$, is obtained by distilling the above-mentioned mixture, and collecting the portion which passes over below 200°. It boils at 166°—172°, and unites quickly with bromine, forming a tetrabromide, from which, however, on exposure to sunshine, crystals of a compound, $C^5H^7Br.Br^4$(*b*) separate, differing from the isomeric body (*a*) in crystalline form, behaviour when heated, and solubility in ether. Hence it appears probable that there are two isomeric tetrabromides of valerylene, $C^5H^8Br^4$ and $C^5H^8Br^2.Br^2$, each of which yields a corresponding substitution-product. Wurtz's diallyl is, perhaps, homologous with valerylene.

Bromovalerylene, C^5H^7Br.—When the above-mentioned mixture of dibromide and tetrabromide of valerylene is distilled to dryness with alcoholic potash-solution, and the distillate mixed with water, a heavy oil separates, which is resolved by fractional distillation into the three following compounds:—(1) *Dibromide of valerylene,* $C^5H^8Br^2$ (boiling at 170°—175°), mixed with a small quantity of the compound $C^5H^8Br(C^2H^3O)$; (2) *Bromovalerylene,* C^5H^7Br, boiling at 125°—130°; and (3) *Valylene,* C^5H^6, boiling at 45° to 50°, together with a small quantity of valerylene. The formation of these bodies is represented by the equations:

$C^5H^8Br^2 - HBr = C^5H^7Br$. Bromovalerylene.
$C^5H^8Br^4 - 2HBr = C^5H^6$. Valylene.
$C^5H^8Br^2 - Br^2 = C^5H^8$. Valerylene.

Bromovalerylene is partially decomposed by distillation, and becomes coloured by keeping. It unites at low temperatures with bromine, forming the compounds $C^5H^7Br^3$ and $C^5H^7Br^5$. When shaken up with an ammoniacal solution of *cuprous chloride*, it is immediately converted into a yellow solid body, consisting of cuprous valylide, C^5H^5Cu, together with cuprous bromide and oxide:

$$C^5H^7Br + Cu^2O = C^5H^5Cu + CuBr + H^2O.$$

VALERYL-HYDRIDE. Syn. with VALERAL (p. 973.)

VALERYLUREA. See CARBAMIDES (i. 753).

VALONIA. The commercial name of the large cups of the prickly-cupped oak (*Quercus Ægilops*), an infusion of which is used in tanning leather. They contain tannin and gallic acid. The tannin does not yield pyrogallic acid by dry distillation, and is but slightly precipitated by sulphuric acid, even from very concentrated solutions.

VALYL. Kolbe's name for TETRYL or BUTYL.

VALYLENE. C^5H^6. (Reboul, Ann. Ch. Pharm. cxxxv. 372; Jahresb. 1865, p. 510.)—This hydrocarbon is found, as above mentioned, among the products of the action of alcoholic potash on dibromide of valerylene, passing over on distillation, together with a little valerylene, between 45° and 50°. It may be obtained pure by treating the mixture with ammoniacal cuprous chloride, which converts the valylene into cuprous valylide, C^5H^5Cu, but does not act upon the valerylene. The cuprous valylide (which may also be obtained by the action of ammoniacal cuprous chloride on bromovalerylene), is washed by decantation with ammoniacal water, then with a little alcohol, and dried. It decomposes quickly when heated, leaving a black residue. It is decomposed by bromine with inflammation, and by fuming nitric acid with incandescence. An ammoniacal silver-solution converts it into a silver-compound of analogous composition and properties.

To separate the valylene, the copper-compound is warmed with a very slight excess of dilute hydrochloric acid, and the hydrocarbon which distils over is condensed by a freezing mixture. Valylene is a light liquid boiling at about 50°, having an alliaceous odour, recalling also that of prussic acid. When brought in contact by drops with *bromine* in a freezing mixture, it forms a crystalline mass saturated with a thick liquid, the crystalline portion consisting of bromide of valylene, $C^5H^6Br^6$, and the liquid being a mixture of the compounds $C^5H^6Br^6$, $C^5H^6Br^4$, and perhaps $C^5H^6Br^2$.

VALYLIDES. See the last article.

VANADATES.
VANADIC ACID. } See Vanadium, Oxides of (p. 989).

VANADINBRONZITE. This name is given by Schafhäutl (N. Jahresb. f. Min. 1844, p. 721) to a mineral from the Serpentine of Bracco, on the coast of Genoa, containing 49·50 per cent. silica, 5·55 alumina, 18·13 lime, 14·12 magnesia, 3·28 ferrous oxide, 3·65 vanadium-pentoxide, 3·75 soda, and 1·77 water. It is coarsely laminar, with one distinct and two indistinct directions of cleavage, has a nacreous lustre and greenish-grey colour, and is translucent in thin laminæ. Hardness less than 4. Specific gravity = 3·255.

VANADINITE. *Vanadate*, or more properly, *Vanadato-chloride of lead.* See Vanadates (p. 991).

VANADIOUS ACID.
VANADITES. } See Vanadium, Oxides of (p. 988).

VANADIUM. *Atomic weight*, 51·2; *Symbol*, V.—A metal usually classed with molybdenum and tungsten, but shown by recent investigations to belong to the same series as arsenic, antimony, and bismuth.

Del Rio, in 1801 (Gilb. Ann. lxxi. 7), found in the lead-ore of Zimapan, in Mexico, a new metal which he designated as *erythronium*; subsequently, however, he regarded it as impure chromium.—Sefström, in 1830 (Pogg. Ann. xxi. 43) found in the bar-iron obtained from the ores of Taberg in Sweden, and especially in the refinery slags, a new metal which he named vanadium, after the Scandinavian deity *Vanadis*; Wöhler (*ibid.* xxi. 49) then showed that the lead-ore of Zimapan consisted of lead-vanadate, and that Del Rio's erythronium was not chromium, but vanadium. Subsequently this metal has been found in several other ores, most abundantly in lead-vanadate from Wanlockhead in Scotland, and from La Plata; in smaller quantity also in pitchblende, in many iron-ores, and the pig-iron obtained from them; also on the native copper of Lake Superior, probably as phosphate; and in several kinds of clay, to the amount of 0·02 to 0·07 per cent. Vanadium appears, therefore, to be somewhat widely diffused, but it never occurs in large quantity, and has, indeed, been hitherto regarded as one of the rarest of the metals. Quite recently, however, a more productive source of it has been discovered by Roscoe (Proc. Roy. Soc. xvi. 223) in some of the copper-bearing beds of the Lower Keuper sandstone of the Trias, worked at Alderley Edge and Mottram St. Andrews, in Cheshire. In working up a pure cobalt-ore from Mottram, a large quantity of a lime-precipitate was obtained, containing nearly 2 per cent. of vanadium.

Extraction.—1. From the refinery slag of the Taberg iron-ore.—The finely-pulverised slag is deflagrated with nitre and carbonate of sodium; the fused mass is digested with boiling water; and into the crude solution of potassium-vanadate thus obtained, lumps of sal-ammoniac are introduced, whereby vanadate of ammonium, which is insoluble in a saturated solution of sal-ammoniac, is deposited in crystalline grains. This salt, when ignited in an open vessel, leaves pure vanadium-pentoxide. (Berzelius.)

2. From certain kinds of pig-iron.—The grey pig-iron smelted from the oolitic iron-ores of Westbury, in Wiltshire, contains, according to Riley (Chem. Soc. J. xvii. 21), about 0·7 per cent. vanadium, which becomes concentrated in the graphitic residue left on dissolving the iron in hydrochloric acid. On treating this residue with potash-ley, to free it from silica, and burning the remaining graphite with free access of air, a mixture of tetroxide and pentoxide of vanadium is obtained. (Riley.)

3. From native vanadate of lead.—The solution of the mineral in nitric acid is freed from lead and arsenic by sulphydric acid; the blue filtered liquid is boiled for a short time, and then evaporated to dryness at a moderate heat; the dark-red residue is boiled with a saturated solution of ammonium-carbonate, which is added from time

to time; and the liquid is filtered at the boiling heat. On cooling, it deposits white needles of ammonium-vanadate, which may be purified by recrystallisation. (Johnston, N. Edinb. J. of Sc. v. 166, 318.)

4. From the lime-precipitate, obtained, as already mentioned, in working the cobalt-ore of Mottram in Cheshire.—This precipitate, containing mainly arsenic, iron, lead, copper, vanadium, and lime, with sulphuric and phosphoric acids, was first well furnaced with ground coal, to drive off the greater portion of the arsenic; then roasted with one quarter of its weight of soda-ash, so as to convert the vanadium into a soluble vanadate; and on lixiviation, arsenic and the heavy metals were completely thrown down by sulphuretted hydrogen. The deep blue solution was neutralised by ammonia, the precipitated vanadium-oxide dried and oxidised by nitric acid, and the crude vanadic acid thus obtained was boiled out with a saturated solution of ammonium-carbonate. The slightly soluble ammonium-vanadate was washed and recrystallised. In order to prepare pure vanadic acid from this salt, it was roasted, and the powdery acid thus obtained was suspended in water into which ammonia-gas was passed; the dissolved ammonium-vanadate was separated by filtration from a residue containing silica, phosphates, &c. The pentoxide obtained by heating this salt was free from phosphorus. A second method of preparing the pure vanadium-pentoxide consists in decomposing the pure oxychloride with water, and freeing the acid from any traces of silica by exposure to hydrofluoric acid gas. Great difficulty was experienced in obtaining vanadium free from phosphorus; all the native vanadates contain large quantities of phosphorus. (Roscoe.)

Metallic vanadium remains when vanadium-nitride is heated to whiteness in ammonia-gas (Uhrlaub, Pogg. Ann. ciii. 134), but it does not appear to have been obtained quite pure.

Berzelius, by igniting vanadium-pentoxide with potassium, and washing out the fused mass with water, obtained a brilliant metallic-looking powder, which has been hitherto regarded as pure vanadium; but Roscoe has shown that it is an oxide.

Compounds of Vanadium.—Berzelius, to whose elaborate research published in 1831 (Pogg. Ann. xxii. 1), we were till lately indebted for nearly all our knowledge of the vanadium-compounds, obtained three oxides, to which he assigned the formulæ VO, VO^2, VO^3 ($V = 68{\cdot}5$, $O = 8$); he also obtained a chloride corresponding to the highest oxide, namely VCl^3. According to these results, vanadium was regarded as a metal belonging to the same class as chromium, molybdenum, and tungsten. This view, however, was somewhat difficult to reconcile with the observed fact of the isomorphism of certain vanadium-compounds with analogous compounds belonging to the phosphorus and arsenic groups; the mineral vanadinite, for example, which is a compound of lead-vanadate and lead-chloride, is isomorphous with apatite, pyromorphite, and mimetesite—minerals consisting of calcium-phosphatochloride, lead-phosphatochloride, and lead-arsenatochloride. This anomaly induced several chemists to suspect that vanadium might really belong to the phosphorus and arsenic group of elements. Baumgarten, in particular (Jahresb. 1865, p. 219), was led to this conclusion by observing among the last crystallisations from the soda mother-liquors at Schöningen, colourless crystals, consisting of phosphatofluoride of sodium, $2Na^3PO^4.NaF.19H^2O$, in which the phosphorus was partly replaced by arsenic, and to a greater extent by vanadium (the crystals containing from 0·89 to 1·06 per cent. vanadic oxide). Baumgarten likewise obtained perfectly similar crystals, containing the same proportion of vanadium, by direct synthesis.

Such observations could not, however, be regarded as having much weight against the definite experimental results of Berzelius, which showed beyond doubt that, if the lowest of the three oxides obtained by him is a monoxide, VO, the highest must be a trioxide, VO^3. This conclusion was based:—1. On the constant loss of weight which the highest oxide undergoes on reduction in hydrogen at a red heat.—2. On the action of chlorine on this reduced oxide, whereby a volatile chloride is formed, and a residue of vanadic oxide obtained, which is found to be exactly one-third of the quantity originally taken for reduction in hydrogen. These results may be represented by the following equations:

$$(1)\quad VO^3 + H^2 = VO + H^2O^2$$
$$(2)\quad 3VO + Cl^6 = VO^3 + 2VCl^3.$$

But the recent experiments of Roscoe, whilst fully confirming these fundamental results of Berzelius, and proving that if the atomic weight assigned to vanadium by that chemist, viz. 68·5, be correct, the formulæ of the oxides must be VO, VO^2, VO^3, or V^2O, V^2O^2, V^2O^3, and that of the volatile chloride VCl^3, have shown, on the other hand,—1. That the supposed metal of Berzelius is really an oxide.—2. That the quantities of oxygen in this and the three higher oxides, united with the same weight of vanadium, are to one another as the numbers 2, 3, 4, 5—these four oxides being, in fact, represented by the formulæ V^2O^2, V^2O^3, V^2O^4, V^2O^5, analogous to those of the oxides of nitrogen (neglecting the monoxide).—3. That the supposed trichloride obtained by Berzelius is an oxychloride, $VOCl^3$, related to vanadic oxide, V^2O^5, in the same manner as phosphoric oxychloride is related to phosphoric oxide. The quantitative results of the reduction of vanadic oxide in hydrogen, and the treatment of the reduced oxide by chlorine, are represented on this view by the equations:

$$V^2O^5 + 2H^2 = V^2O^3 + 2H^2O.$$
$$3V^2O^3 + 6Cl^2 = V^2O^5 + 4VOCl^3.$$

Roscoe has further pointed out that vanadic oxide forms, with metallic oxides, two classes of salts, analogous in composition to the orthophosphates and metaphosphates (p. 991). It may therefore be concluded that vanadium exhibits in all respects the characters of a metal belonging to the phosphorus and arsenic group.

VANADIUM, BROMIDES OF. No bromide of vanadium has yet been obtained in the free state. The so-called tribromide obtained, by Schafarik, is an oxybromide, $VOBr^3$ (p. 992).—The *tetrabromide*, VBr^4, is probably contained in the blue solution of vanadium-tetroxide in hydrobromic acid. This solution dries up in a vacuum to a blue gum, which becomes violet-brown when heated, but is still perfectly soluble in water. The aqueous solution gives off a greenish-grey precipitate with ammonia.

VANADIUM, CHLORIDES OF. None of these compounds are known in the free state.—The *tetrachloride*, VCl^4, probably exists in solution and in two isomeric modifications:

α. Vanadic acid, boiled with strong hydrochloric acid, gives off chlorine and forms a blue solution, which, when concentrated by evaporation, yields a blue syrup not precipitated by alcohol. When perfectly dried by heat, it leaves a brown oxychloride no longer quite soluble in water.

β. Vanadium-tetroxide dissolved in strong hydrochloric acid forms a brown solution, which, when left to evaporate, yields a black liquid, becoming brown again on dilution. The brown solution turns blue when evaporated by heat, or on addition of strong sulphuric acid. Ammonia added to the brown solution forms a greenish-brown precipitate, insoluble in water.

Several oxychlorides of vanadium have been obtained (p. 992).

VANADIUM, DETECTION AND ESTIMATION OF. 1. *Blowpipe Reactions.*—All compounds of vanadium heated with *borax* or *phosphorus-salt*, produce a clear bead, which is colourless if the quantity of vanadium is small, yellow if it is large; in the inner flame the bead acquires a beautiful green colour.

2. *Reactions in Solution.*—Vanadium-dioxide (the metallic vanadium of Berzelius), may be obtained in solution by the action of nascent hydrogen on a solution of the pentoxide in sulphuric acid. The solution of hypovanadious sulphate thus obtained has a lavender colour, and is an extremely powerful reducing agent. (See p. 987.)

Vanadium-tetroxide, or vanadious oxide (the dioxide of Berzelius) dissolves in acids, forming salts called vanadious salts, most of which are of a blue colour. Vanadious salts form, with the *hydrates* and *monocarbonates* of the *fixed alkalis*, a greyish-white precipitate of hydrated vanadious oxide, which dissolves in a moderate excess of the reagent, but is precipitated by a large excess, in the form of a vanadite of the alkali-metal.—*Ammonia* in excess produces a brown precipitate, soluble in pure water, but insoluble in water containing ammonia.—*Ferrocyanide of potassium* forms a yellow precipitate, which turns green on exposure to the air.—*Sulphuric acid* produces no precipitate.—*Sulphide of ammonium* forms a black-brown precipitate, soluble in excess.—*Tincture of galls* forms a finely-divided black precipitate, which gives to the liquid the appearance of ink.

Vanadium-tetroxide also unites with the more basic metallic oxides, forming salts called vanadites, all of which are insoluble, except those of the alkali-metals. The solutions of the alkaline vanadites are brown, but when treated with *sulphydric acid*, they acquire a splendid red-purple colour, arising from the formation of a sulphur-salt.—*Acids* colour them blue, by forming a double vanadious salt; *tincture of galls* colours them blackish-blue. The insoluble vanadites, when moistened or covered with water, become green, and are converted into vanadates.

Vanadium-pentoxide, or vanadic oxide, reacts for the most part as an acid oxide, uniting with bases to form salts called vanadates. These salts are all more or less soluble in water; the barium- and lead-salts, however, are very sparingly soluble. The alkaline vanadates are sparingly soluble in cold water, especially if it contains free alkali or another alkaline salt: *e.g.*, vanadate of ammonium is nearly insoluble in water containing sal-ammoniac: hence, on treating a solution of potassium-vanadate with excess of sal-ammoniac, a precipitate of ammonium-vanadate is produced.

The aqueous solutions of the vanadates are coloured red by the stronger acids, but the mixture often becomes colourless again after a while. They give orange-red precipitates with the *antimonious, plumbic, cupric,* and *mercuric salts.*—*Sulphydric acid* produces, in neutral solutions of the vanadates, a mixed precipitate of sulphur and hydrated vanadious oxide; in acid solutions it merely throws down sulphur, and reduces the vanadic oxide to vanadious oxide.—*Sulphide of ammonium* imparts to solutions of the vanadates a brown-red colour, and, on adding an acid to the solution, a light-brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur; the liquid, at the same time, generally acquires a blue colour.

Vanadic and chromic acids are the only acids whose solutions are red; they are distinguished from one another by the vanadic acid becoming blue, and the chromic acid green, by deoxidation.

When a solution of vanadic acid, or an acidulated solution of an alkaline vanadate, is shaken up with ether containing *hydric peroxide,* the aqueous solution acquires a red colour, like that of ferric acetate, while the ether remains colourless. This reaction will serve to detect the presence of 1 pt. of vanadic acid in 40,000 pts. of liquid. The red colouring is also produced by ozonised oil of turpentine, and by hydric peroxide alone; also by ordinary ether not containing hydric peroxide. Chromic acid, even in considerable quantity, does not interfere with the reaction. (G. Werther, J. pr. Chem. lxxxiii. 195.)

3. *Estimation and Separation.*—Vanadium, in the form of free pentoxide or tetroxide, is estimated by reducing it to trioxide by ignition in a stream of hydrogen.

In solutions of vanadites, the vanadium is precipitated by mixing the solution with excess of mercuric chloride, and then with ammonia. The precipitate, consisting of mercuric vanadite and chloride of dimercurammonium (white precipitate) is ignited in contact with the air, whereupon vanadium-pentoxide remains mixed only with a small quantity of mercuric oxide, from which it is separated by solution in carbonate of ammonia.

When vanadic acid is dissolved in a liquid not containing any other fixed constituents, it may be separated as vanadium-pentoxide by evaporation, and if volatile acids or ammonia are also present, by igniting the residue.

Vanadic acid may be separated from many acids and other substances, by causing it to unite with ammonia, expelling the excess of ammonia by evaporation, and then adding a saturated solution of sal-ammoniac, in which vanadate of ammonia is insoluble. The precipitate is then washed on a filter, first with solution of sal-ammoniac, then with alcohol, and the ammonia driven off by ignition. This method serves to separate vanadium from the alkali-metals.

Vanadium may be separated from many of the preceding metals by the solubility of its sulphide in sulphide of ammonium; and from others, which are precipitated from their acid solutions by sulphydric acid, by acidulating the liquid and passing sulphydric acid gas through it; the vanadium then remains dissolved in the form of vanadious oxide.

From *lead, barium,* and *strontium,* vanadic acid may be separated by fusion with acid sulphate of potassium; on treating the fused mass with water, sulphate of lead, barium, or strontium remains, while vanadate of potassium is dissolved. Sulphuric acid cannot be used to effect this separation, because the precipitated sulphate always carries down with it a portion of the vanadium. (Berzelius.)

Vanadium may also be separated from these metals, and from all others which form insoluble carbonates, by fusing the vanadate with twice its weight of sodium-carbonate, digesting the fused mass in water, and washing the undissolved portion. (v. Hauer, J. pr. Chem. lxix. 385.)

Atomic Weight of Vanadium.—The atomic weight of this metal has been determined in two ways:—*a.* By igniting vanadium-pentoxide, V^2O^5, in pure dry hydrogen-gas, whereby it is reduced to the trioxide, V^2O^3. The atomic weight of vanadium is then determined from he equation:

$$V = \frac{8\,(5b-3a)}{a-b},$$

where a = the weight of vanadium-pentoxide taken;
„ b = „ vanadium-trioxide obtained.

Roscoe, in four experiments, obtained the following results:

No.	Weight of pentoxide taken.	Weight of trioxide obtained.	Atomic weight of vanadium.
1.	7·7397	6·3827	51·26
2.	6·5819	5·4296	51·39
3.	5·1895	4·2819	51·48
4.	5·0450	4·1614	51·35

The mean atomic weight deduced from these experiments is 51·37, with a mean error of ± 0·066. Berzelius found, as a mean of four experiments, that 120·927 pts. of the pentoxide yielded 100 pts. of trioxide, which gives, according to the above equation, V = 52·55.[*] The difference is probably due to the fact that the vanadium employed by Berzelius contained a trace of phosphorus, which prevented the complete reduction.

β. By the analysis of vanadium-oxytrichloride or vanadyl-trichloride, $VOCl^3$.—The chlorine in this compound was estimated both by Gay-Lussac's volumetric process, and by weight-analysis. Nine volumetric determinations give 61·306 per cent. chlorine; seven gravimetric determinations give 61·241 per cent. From these numbers an atomic weight of 51·05 is obtained for vanadium. The mean of 51·05 and 51·37 (the number obtained from the reduction experiments), viz. 51·21, is regarded as the true atomic weight of vanadium. (Roscoe.)

VANADIUM, FLUORIDES OF. Vanadium-tetroxide dissolves in hydrofluoric acid, forming a blue solution, which yields, by spontaneous evaporation, a greenish syrup and green crystals, probably consisting of the hydrated tetrafluoride. It forms light-blue double salts with the fluorides of potassium and sodium.

Vanadium-pentoxide also dissolves in warm aqueous hydrofluoric acid, and the solution, evaporated at 40°, leaves a white mass, which dissolves perfectly in water, but, when strongly heated, leaves an insoluble residue of pure vanadium-pentoxide.

VANADIUM, IODIDES OF. Vanadium-tetroxide dissolves in aqueous hydriodic acid, forming a blue solution, which turns green in contact with the air, and yields, by spontaneous evaporation, a brown semifluid mass, soluble with black-brown colour in water.

VANADIUM, NITRIDES OF. There are two compounds of vanadium and nitrogen.—The *mononitride*, VN, obtained by heating the compound of vanadium-oxytrichloride with ammonium-chloride to whiteness, in a current of ammonia-gas, is a greyish-white powder, unalterable in the air. It gave, by analysis, 78·6 per cent. vanadium and 21·4 nitrogen, the formula VN requiring 77·8 vanadium and 20·2 nitrogen. (Roscoe.)

Vanadium-dinitride, VN^2, was obtained by Uhrlaub (Pogg. Ann. ciii. 134), who however assigned to it a different formula, by heating the ammonium-oxychloride in ammonia-gas to a moderate temperature. It is a black powder, which is strongly acted upon by warm nitric acid, and gives off ammonia when fused with potash.

VANADIUM, OXIDES OF. The oxides of vanadium are analogous in composition to the oxides of nitrogen, excepting that the one corresponding to the protoxide or monoxide of nitrogen has not yet been obtained. The complete series is as follows:

Vanadium-monoxide (hyp.)	V^2O
Vanadium-dioxide, Hypovanadious oxide, or Vanadyl	V^2O^2
Vanadium-trioxide, or Hypovanadic oxide	V^2O^3
Vanadium-tetroxide, Vanadious oxide, or Vanadious anhydride	V^2O^4
Vanadium-pentoxide, Vanadic oxide, or Vanadic anhydride	V^2O^5

Vanadium-dioxide, V^2O^2.—This, the lowest oxide of vanadium yet obtained, was regarded by Berzelius as metallic vanadium. As it enters into many vanadium-compounds (just as uranyl enters into the uranic compounds), it may be appropriately called vanadyl.

Vanadium-dioxide is obtained by reducing either of the higher oxides with potassium (Berzelius), or by passing the vapour of vanadium-oxytrichloride, ($VOCl^3$), mixed with excess of hydgogen, through a combustion-tube containing red-hot charcoal (Schafarik, Ann. Ch. Pharm. cix. 85; Jahresb. 1859, p. 168). As obtained by the second process, it forms a light-grey glittering powder, or a metallically lustrous crystalline crust, having a specific gravity of 3·64, brittle, very difficult to fuse, and a conductor of electricity. When heated to redness in the air, it takes fire and burns to black oxide. It is insoluble in sulphuric, hydrochloric, and hydrofluoric acid, but dissolves easily in nitromuriatic acid, forming a dark-blue liquid. (Schafarik.)

The dioxide may be prepared in solution by the action of nascent hydrogen, evolved by metallic zinc, cadmium, or sodium-amalgam, on a solution of vanadic acid in sulphuric acid. After passing through all shades of blue and green, the liquid acquires a permanent lavender tint, and then contains the vanadium in solution as dioxide, or as hypovanadious salt. This compound absorbs oxygen more rapidly than any other

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[*] Berzelius, regarding the highest oxide as VO^3, $[O = 8]$ and supposing it to be reduced to VO by ignition in hydrogen, calculated the atomic weight of the metal from the equation $V = \frac{8(3b - a)}{a - b}$, which gives, according to his experiments, $V = 68·55$, and, according to Roscoe's, $V = 67·37$; this is really the molecular weight of the dioxide.

The aqueous solutions of the vanadates are coloured red by the stronger acids, but the mixture often becomes colourless again after a while. They give orange-red precipitates with the *antimonious*, *plumbic*, *cupric*, and *mercuric salts*.—*Sulphydric acid* produces, in neutral solutions of the vanadates, a mixed precipitate of sulphur and hydrated vanadious oxide; in acid solutions it merely throws down sulphur, and reduces the vanadic oxide to vanadious oxide.—*Sulphide of ammonium* imparts to solutions of the vanadates a brown-red colour, and, on adding an acid to the solution, a light-brown precipitate is formed, consisting of vanadic sulphide mixed with sulphur; the liquid, at the same time, generally acquires a blue colour.

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Vanadium-pentoxide, V^2O^5. *Vanadic Oxide. Vanadic Anhydride. Anhydrous Vanadic Acid.*—This is the highest oxide of vanadium. It is prepared by igniting vanadate of ammonium in an open platinum-crucible; when cold, it has a rusty-yellow colour, lighter in proportion as the oxide is more finely divided.—The pentoxide may also be obtained by dissolving the impure tetroxide in strong sulphuric acid, and evaporating the solution. Pure vanadic sulphate, $V^2O^5.2SO^3.H^2O$ (p. 617—there called "basic vanadic sulphate," and represented by the formula $VO^3.2SO^3$), then remains as a light, orange-coloured, sandy powder, which, on ignition, leaves the pure pentoxide (Fritzsche, J. pr. Chem. liii. 93).—Very pure vanadium-pentoxide is likewise obtained by decomposing vanadyl-trichloride with water (Schafarik):

$$2VOCl^3 + 3H^2O = V^2O^5 + 6HCl.$$

Pure vanadium-pentoxide has a more or less reddish-yellow colour: it is tasteless, reddens moistened litmus-paper, and dissolves in 1,000 pts. of water, forming a light-yellow solution. When heated, it melts without decomposition, if kept from contact with deoxidising substances; and the red liquid crystallises on cooling, becoming incandescent at the moment of solidification, in consequence of the heat then suddenly evolved. The solidified mass is yellowish-red, and according to Nordenskjold (Pogg. Ann. cxii. 160), contains more or less distinct rhombic crystals.

Vanadium-pentoxide is not altered by simple ignition, but is easily reduced by heating with potassium, charcoal, hydrogen, carburetted hydrogen, organic substances, &c. In solution, it is also easily reduced by sulphurous or sulphydric acid, and even by nitrous acid; also by stannous salts, and by sugar, alcohol, and other organic substances, the colour of the solution then changing from red or yellow to green and blue. The solution of the acid in hydrochloric acid gives off chlorine when evaporated; tincture of galls colours the solution of vanadic acid black, on standing, in consequence of reduction.

Vanadic Hydrate or *Vanadic Acid*, $H^2O.V^2O^5$ + aq. or $2HVO^3.H^2O$, is obtained, by treating a somewhat concentrated solution of an anhydrovanadate of alkali-metal with nitric acid, as a bulky flocculent precipitate, which dries up in the air to a light brown-red powder having the composition just mentioned. It gives off 1 at. water over oil of vitriol, and when dried by heat, forms solid lumps, having a conchoïdal fracture.

Vanadium-pentoxide dissolves in the stronger acids, forming red or yellow solutions, which are partly decolorised by boiling and evaporation, especially when they contain excess of vanadium; many of these solutions yield crystalline compounds by spontaneous evaporation. (See Phosphatovanadic Acid, iv. 686; and Sulphates of Vanadium, v. 617). Alkalis added to the solutions, form precipitates soluble in excess. The solutions are easily reduced by oxidisable substances.

Vanadates.—Vanadium-pentoxide unites with bases much more readily than with acids. When fused with alkaline carbonates, it eliminates 3 at. carbonic anhydride, forming orthovanadates, analogous to the orthophosphates, *e.g.*:

$$3(Na^2O.CO^2) + V^2O^5 = 3Na^2O.V^2O^5 + 3CO^2.$$

It also forms metavanadates, analogous to the metaphosphates, and two series of acid vanadates or anhydrovanadates, viz.:

$$\begin{array}{llll}
\text{Orthovanadates, } M^3VO^4 & = \left.\begin{matrix}(VO)'''\\ M^3\end{matrix}\right\}O^3 & = & 3M^2O.V^2O^5.^* \\
\text{Metavanadates, } MVO^3 & = \left.\begin{matrix}(VO)'''\\ M\end{matrix}\right\}O^2 & = & M^2O.V^2O^5. \\
\text{Divanadates, } M^2V^4O^{11} & = 2MVO^3.V^2O^5 & = & M^2O.2VO^5. \\
\text{Trivanadates, } M^2V^6O^{16} & = 2MVO^3.2V^2O^5 & = & M^2O.3V^2O^5.
\end{array}$$

Metavanadate of lead occurs native, as *Dechenite*; the orthovanadate also, combined with lead-chloride, as *Vanadinite*. *Descloizite* is a diplumbic vanadate, $Pb^2V^2O^7 = 2PbO.V^2O^5$, analogous in composition to a pyrophosphate.

The metavanadates are mostly yellow; some of them however, especially those of the alkaline earth-metals, and of zinc, cadmium, and lead, are converted by warming—either in the solid state, or under water, or in aqueous solution, especially in presence of a free alkali or alkaline carbonate—into isomeric colourless salts. The same transformation takes place also, though more slowly, at ordinary temperatures. The metavanadates of alkali-metal are colourless. The acid vanadates are yellow, or yellowish-red, both in the solid state and in solution; hence the solution of a neutral vanadate becomes yellowish-red on addition of an acid. The metavanadates of known reducing agent, and bleaches indigo and other vegetable colours as quickly as chlorine. (Roscoe.)

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* $3MO.VO^3$, according to the old atomic weights.

The degree of oxidation of the vanadium in the lavender-coloured solution was ascertained by oxidising it with a standard solution of permanganate. By this method it was found that 150 pts. of vanadium-pentoxide lost 26·53 per cent. oxygen on reduction with zinc; the calculated loss from V^2O^5 to V^2O^2 is 26·3.

When the neutral lavender-coloured solution of a hypovanadious salt is left exposed to the air for a few seconds, the colour changes to a deep chocolate-brown from absorption of oxygen; indeed, this reaction is as delicate as that of an alkaline pyrogallate. If air be passed through the acid lavender-coloured solution of hypovanadious sulphate, oxygen is absorbed, the liquid assumes a permanent blue colour, and the vanadium is then contained in solution as tetroxide. If the free acid contained in the lavender solution be neutralised by zinc, the liquid, on exposure to air, attains a permanent brown tint, which, on addition of acids, becomes green, the solution then containing vanadium-trioxide. (Roscoe.)

Vanadium-trioxide, V^2O^3, or **Vanadyl-monoxide,** $(V^2O^2)''O$. (Berzelius's suboxide).—Obtained by igniting the pentoxide in hydrogen-gas, or in a crucible lined with charcoal. It is a black powder, with an almost metallic lustre, and infusible; by pressure it may be united into a coherent mass which conducts electricity (Schafarik). When exposed warm to the air, it glows, absorbs oxygen, and is converted into pentoxide. At ordinary temperatures, it slowly absorbs oxygen, and is converted into tetroxide. By ignition in chlorine-gas it is converted into vanadyl-trichloride and vanadium-pentoxide. It is insoluble in acids, but may be obtained in solution by the reducing action of nascent hydrogen evolved from metallic magnesium on a solution of vanadic acid in sulphuric acid. 100 pts. of vanadium-pentoxide were found to lose, on reduction with magnesium, 17·7 per cent. oxygen; the calculated loss, on reduction to V^2O^3, is 17·5 per cent. Solutions of vanadium-trioxide may also be obtained by partial oxidation of the lavender-coloured solution of the dioxide (Roscoe). According to Schafarik, vanadium-trioxide unites with acids, forming salts (which may be called hypovanadic salts), red in the anhydrous, and green in the hydrated state. When the tetroxide or pentoxide is ignited in a glass-tube in a stream of hydrogen, the glass acquires a red colour, in consequence of the formation of hypovanadic silicate.

Vanadium-tetroxide, V^2O^4. *Vanadious Oxide* or *Anhydride*. (Berzelius's vanadic oxide.)—This oxide is produced, either by the oxidation of the dioxide or trioxide, or by the partial reduction of the pentoxide. By allowing the trioxide to absorb oxygen at ordinary temperatures, the tetroxide is obtained in blue shining crystals. It dissolves in acids, the more easily in proportion as it has been less strongly ignited, forming solutions of vanadious salts, which have a bright-blue colour. The same solutions are produced by the action of moderate reducing agents, such as sulphurous, sulphydric, or oxalic acid, upon vanadic acid in solution; also by passing air through acid solutions of the dioxide till a permanent blue colour is attained. 100 pts. of vanadium-pentoxide, reduced with sulphurous or sulphydric acid, lose 9·03 per cent.; the calculated loss on reduction to the tetroxide is 8·75 per cent. (Roscoe.)

The principal reactions of vanadious salts have been already mentioned (p. 985). The solutions treated with alkaline carbonates, yield a precipitate of vanadious hydrate, which, when dried out of contact with the air, is neutral, has a grey colour, and is insoluble in water. It oxidises readily in contact with the air, acquiring a brown colour and acid reaction, and imparting a green colour to water. It dissolves easily in acids, and, when ignited, leaves the anhydrous tetroxide.

Vanadious phosphate and sulphate have been obtained in definite crystals (iv. 586; v. 617).

Vanadium-tetroxide also unites with the more basic metallic oxides, forming salts called vanadites. Those of the alkali-metals are soluble in water, and are formed by dissolving the tetroxide or the corresponding hydrate in caustic alkalis; the rest are insoluble and are obtained by precipitation.—The *ammonium-salt* is likewise produced by adding ammonia to a warm solution of a vanadious salt (the sulphate, for example), till the resulting precipitate redissolves with black-brown colour. This solution, if left to itself in a well-closed vessel, deposits vanadite of ammonium on cooling, as a brown crystalline powder, the liquid then becoming colourless. The salt dissolves in pure water, forming a brown solution, from which it is precipitated by ammonia.—The *potassium-salt*, prepared in a similar manner, forms brown shining crystals.

The insoluble vanadites have been but little examined.—The *manganous salt* is a brown powder, which, when exposed to the air in the moist state, oxidises to manganous vanadate.—The *mercuric salt* is thrown down, together with chloride of dimercurammonium (white precipitate), on adding ammonia to a solution of mercuric chloride mixed with a vanadous salt. The precipitate, when ignited, leaves vanadium-tetroxide, still retaining a small quantity of mercuric oxide.

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* $3MO.VO^3$, according to the old atomic weights.

Vanadates containing fixed bases are not decomposed by ignition; strong *acids* turn their solutions red, and when added in excess, often throw down very acid salts. From concentrated solutions of acid vanadates, *nitric acid* throws down a bulky brown precipitate of vanadic acid, retaining a small quantity of the base.—*Hydrochloric acid* decomposes the vanadates, with evolution of chlorine and formation of vanadium-tetroxide.—*Acetic acid*, in excess, takes away part of the base from neutral vanadates, converting them into di- and tri-vanadates.—*Sulphurous acid*, *alcohol*, and other reducing agents, colour the acid solutions blue, by formation of vanadium-tetroxide.

The vanadates have been examined chiefly by **Berzelius**, and more recently by v. **Hauer** (J. pr. Chem. lxix. 385; lxxvi. 156, 929; lxxx. 324), and **Czudnowicz** (Pogg. Ann. cxx. 17; Jahresb. 1863, p. 221); their crystalline forms by **Grailich** (*Krystallographische Untersuchungen*, Wien u. Olmütz, 1858, p. 3).

Vanadates of Ammonium.—The *metavanadate*, $(NH^4)VO^3$, is obtained by adding an excess of ammonia to the reddish-yellow acid solution of vanadic acid in ammonia, then warming it and leaving it to evaporate, or mixing it with alcohol; also by placing a lump of sal-ammoniac, more than sufficient for saturation, in a solution of potassium- or sodium-vanadate (p. 985). It separates in colourless, transparent, crystalline crusts, which dissolve slowly in cold water, forming a colourless liquid; quickly in boiling water, forming a yellow solution. It is decomposed by heat, leaving vanadium-pentoxide when heated in contact with the air. Its solution forms, with tincture of galls, a deep black liquid, which may be used as an insoluble ink. Alkalis do not act upon it; acids colour it blue; chlorine destroys the black colour, but the ink does not fade spontaneously (**Berzelius**).—*Yellow metavanadate.*—The yellow solution of vanadic acid in ammonia mixed with excess of ammonia, and left to evaporate *without warming*, yields lemon-yellow indistinct crystals, which dissolve in water with the same colour, and are reprecipitated therefrom by alcohol.

The *divanadate*, $2(NH^4)VO^3.V^2O^5.4H^2O$ or $(NH^4)^2O.2V^2O^5.4H^2O$, is obtained by saturating warm aqueous ammonia with vanadic acid, and leaving it to evaporate; or by mixing a boiling solution of the metavanadate, gradually and with agitation, with acetic acid, till the precipitate redissolves. The yellowish-red liquid, on cooling, deposits the salt in large, transparent, orange-red crystals, which dissolve in water, and are precipitated by alcohol as a lemon-yellow powder.—This *trivanadate*, $(NH^4)VO^3.V^2O^5.3H^2O$ or $(NH^4)^2O.3V^2O^5.6H^2O$, is obtained by repeated crystallisation of the diacid salt from water containing acetic acid. It forms large splendid red crystals, which are permanent in the air, more soluble in water than the preceding salt, but give off water and ammonia at a moderate heat. (v. **Hauer**.)

Vanadates of Barium.—The *metavanadate*, $Ba''(VO^3)^2.H^2O$, is obtained, by double decomposition, as a yellow gelatinous precipitate, which turns white slowly in the cold, immediately when heated. The white and yellow salts, which have the same composition, dissolve sparingly in water, each with its own colour, and the solution, when left to evaporate, deposits the salt in white crystalline grains. It dissolves with red colour in strong sulphuric acid. When heated, it gives off water, and turns yellow, but becomes white again on cooling. At a red heat, it melts to a yellow-brown transparent mass. It is completely decomposed by fusion with acid sulphate of potassium.—The *divanadate*, $Ba''(VO^3)^2.V^2O^5$, separates by spontaneous evaporation, from a solution of potassium-divanadate mixed with chloride of barium, in orange-yellow prisms, or on addition of alcohol, in shining lemon-yellow scales, slightly soluble in water.—Another *acid salt*, $3BaO.5V^2O^5.19H^2O = 3Ba(VO^3)^2.2V^2O^5.19H^2O$, is obtained by dropping chloride of barium into a warm solution of the divanadate, and then adding acetic acid till the precipitate redissolves. The solution, on cooling, deposits the salt in reddish-yellow, shining, oblique prisms. (v. **Hauer**.)

A so-called *basic salt* (? the orthovanadate) is formed, on mixing the solution of the metavanadate with baryta-water, as a yellow precipitate, which after a while turns white.

Vanadates of Calcium.—The *metavanadate* is obtained, by slow evaporation of ammonium-vanadate mixed with calcium-chloride, in white or yellowish crystalline crusts; it is moderately soluble in water (more soluble than the strontium-salt), and is precipitated by alcohol.—The *acid salt* forms large, orange-red, non-efflorescent crystals, easily soluble in water.—A *basic salt* (? orthovanadate) is said to be obtained by mixing the solution of the metavanadate with lime-water.

Vanadates of Copper.—*Cupric metavanadate* separates, as a yellow precipitate, on adding alcohol to a mixture of a cupric salt and potassium-metavanadate.—An *acid salt* separates, as a yellow crystalline crust, from a solution of acid potassium-vanadate mixed with cupric sulphate.

Cupric orthovanadate occurs native in volborthite, a mineral found at Friedrichsrode in the Thuringian Forest, and at Syssersk and Nischne-Tagilsk in Russia. The mineral from Friedrichsrode contains, according to Credner's analysis (Pogg. Ann. lxxix. 546), 39·02 per cent. V^2O^5, 38·27 CuO, 16·62 CaO, and 5·05 water, together with 0·92 MgO, 0·52 MnO, and 0·76 insoluble matter, agreeing nearly with the formula $(Cu;Ca)^3(VO^4)^2.(Cu;Ca)H^2O^2$; that from Russia appears to be similarly constituted, but to contain only copper without calcium; but it has not been analysed. The specific gravity of the Thuringian mineral is 3·495; that of the Russian, 3·55. Hardness = 3. Both minerals form small six-sided tables, spherical, radiate, granulo-laminar or scaly lumps, or earthy deposits, having an olive-green, grass-green, siskin-green, or lemon-yellow colour, vitreous and nacreous lustre, and yellow or greenish-yellow to greyish streak. The mineral is soluble in nitric acid.

Vanadates of Lead.—The *metavanadate*, $Pb(VO^3)^2$, occurs native as dechenite (ii. 308). It is also obtained by precipitating either the metavanadate or acid vanadate of potassium with acetate of lead. It dissolves slightly with yellow colour in water, easily in dilute nitric acid; when it is heated with strong nitric acid, a brown substance separates, probably consisting of a lead-vanadate containing a very large excess of acid. The metavanadate is not decomposed by boiling with aqueous carbonate of potassium, and not completely by boiling with strong sulphuric acid; but fusion with acid sulphate of potassium decomposes it perfectly.—The *divanadate*, $Pb(VO^3)^2.V^2O^5$, is obtained by precipitating the acid potassium-salt with nitrate of lead, as an orange-yellow precipitate, slightly soluble, with yellow colour, in water.

A *diplumbic vanadate* (pyrovanadate), $Pb^2V^2O^7 = 2PbO.V^2O^5$, occurs native as descloizite.

The *triplumbic salt*, or *orthovanadate*, occurs native in combination with chloride of lead, as vanadinite or vanadite, $PbCl^2.3Pb^3VO^4$, a mineral occurring at Zimapan in Mexico, in the county of Wicklow in Ireland, at Wanlockhead in Scotland, at Windischkappel in Carinthia, and at Beresowsk in the Ural, in crystals belonging to the hexagonal system, isomorphous with pyromorphite and mimetesite. The crystals usually exhibit the combination of the hexagonal prism, ∞P with the basal face oP and the hexagonal pyramid P, having the angle P : P in the terminal edges = 143°. It also forms kidney-shaped lumps, with fusiform to fibrous separation. Colour yellow to brown. Lustre waxy to adamantine. Transparent to translucent on the edges only. Hardness = 3. Specific gravity = 6·8 to 7·2 It dissolves in nitric acid, forming a yellow solution, any undissolved portion becoming covered with a red deposit of vanadium-pentoxide.

Analyses:—*a*. From Zimapan (Berzelius).—*b*. From Wicklow in Ireland (Thomson, *Outlines*, i. 574).—*c*. From Windischkappel: crystallised; specific gravity = 6·886 (Rammelsberg, Pogg. Ann. xcviii. 249).—*d*. From Beresowsk: brown crusts on crystallised pyromorphite; specific gravity = 6·863 (Struve, Verh. d. min. Ges. zu Petersburg, 1857):

	a.	*b.*	*c.*	*d.*	
Chlorine	2·56	2·44	2·23	2·46	
Vanadium-pentoxide .	. . .	23·43	17·41	16·98	14·54
Phosphoric pentoxide .	. . .	. .	0·95	3·08	2·79
Lead-oxide	76·54	73·94	76·70	79·47	78·88
			97·29	101·99	

A *cupricoplumbic vanadate* called chileite, occurring as an amorphous brown substance in cavities of the massive pyromorphite of Mina Grande in Chile, was found by Domeyko (Ann. Min [4], xiv. 145) to contain 15·21 per cent. V^2O^5, 5·26 As^2O^5, 0·72 P^2O^5, 60·56 PbO, 17·88 CuO. and 0·37 $PbCl^2$, which may be represented, approximately, by the formula $(Pb;Cu)^3(VO^4)^2.3(Pb;Cu)O$, the vanadium being partly replaced by arsenic and phosphorus.

Vanadates of Lithium.—The *metavanadate* crystallises from concentrated solutions, in radiate groups of slender colourless needles, easily soluble in water.—The *acid salt* forms large red efflorescent crystals, resembling acid chromate of potassium, easily soluble in water and not completely precipitated by alcohol.

Vanadates of Potassium.—The *metavanadate*, KVO^3 or $K^2O.V^2O^5$, disolves slowly in cold, easily in boiling water, with difficulty in water containing potash. The solution yields, by spontaneous evaporation, a syrup which dries up to a white earthy mass, melting when heated to a transparent yellow liquid, and becoming white again on cooling.—The *acid salt*, $2KVO^3.V^2O^5.3H^2O$, or $K^2O.2V^2O^5.3H^2O$, is obtained by fusing the metavanadate with vanadium-pentoxide, or by boiling it with addition of water. It forms broad, reddish-yellow, crystalline laminæ, slightly soluble in cold, abundantly in boiling water. The crystals, when heated, give off their water, and turn brick-red; the dry salt is easily fusible, and forms a yellow mass on cooling. The salt is partially decomposed by boiling with a small quantity of water, metavanadate and divanadate dissolving, and a more acid salt remaining behind. On mixing a cold concentrated solution of the divanadate with caustic potash, the divanadate partly separates unaltered; but if the two solutions are mixed hot, metavanadate is produced.

Vanadates of Silver.—The *metavanadate* is a gelatinous, yellowish, or whitish precipitate, soluble in nitric acid and in very dilute ammonia, and precipitated from the latter solution by concentrated ammonia. It is not completely decomposed by hydrochloric acid.—The *acid salt* is yellowish-red, slightly soluble in water, easily soluble in nitric acid and in very dilute ammonia. It melts below a red heat, and crystallises on cooling. The ammoniacal solution yields, by evaporation, crystals of ammonio-argentic vanadate.

Vanadates of Sodium.—The *metavanadate* resembles the potassium-salt.—The *divanadate*, $2NaVO^3.V^2O^5.9H^2O = Na^2O.2V^2O^5.9H^2O$, is prepared like the corresponding potassium-salt, and separates, by spontaneous evaporation, in large crystals of a splendid orange-red colour. It is but slightly soluble in water, even at the boiling heat: nevertheless, 1 pt. of it imparts a distinct yellow colour to 200,000 pts. of water It effloresces in dry air, acquiring a rusty-brown colour, melts at an incipient red heat, and forms, on cooling, a shining, amorphous, varnish-like mass of a dark-red colour.

A *phosphatovanadate of sodium* is obtained by heating a mixture of vanadic and sodic phosphates with nitric acid.

Vanadates of Strontium.—The *metavanadate*, $Sr(VO^3)^2$, is gradually precipitated by chloride of strontium from metavanadate of ammonium, in white crystalline grains. It is more soluble than the barium-salt. The solution, mixed with strontia-water, forms, after some time, a yellow precipitate, which afterwards turns white (probably the orthovanadate).—The *divanadate*, $Sr(VO^3)^2.V^2O^5.9H^2O = SrO.2V^2O^5.9H^2O$, separates on cooling from a hot very strong solution of sodium-divanadate mixed with chloride of strontium, in shining orange-red crystals, having the form of sodium-divanadate. It is not very soluble in water, but more soluble than the barium-salt. The crystals do not effloresce even in dry air.—The *trivanadate*, $Sr(VO^3)^2.2V^2O^5.14H^2O = SrO.3V^2O^5.14H^2O$, is prepared by mixing a solution of an alkaline divanadate with acetic acid and strontium-chloride, and heating the liquid nearly to the boiling-point. A straw-yellow basic salt is then deposited, and the deep-red filtrate evaporated over oil of vitriol yields crystals of the trivanadate. By recrystallisation, with addition of a large quantity of free acetic acid, it is obtained pure, in large, red, diclinic crystals, exhibiting a golden-yellow surface-lustre by reflected light. They are permanent in the air, give off 8 at. water at 100°, turn yellow, and melt at a low red heat to a dark-red liquid which solidifies to a crystalline mass on cooling. The salt dissolves easily, and without decomposition, in water, on addition of acetic acid. (v. Hauer, J. pr. Chem. lxxvi. 156.)

Vanadates of Vanadium.—Several oxides of vanadium, intermediate in composition between the tetroxide and pentoxide, and perhaps consisting of compounds of the two, are described by Berzelius. They are produced by direct oxidation of the tetroxide, or by mixing vanadious salts with vanadates in various proportions. The compounds thus characterised are:—1. A purple oxide, formed when vanadious hydrate is left for twenty-four hours in a vessel not perfectly closed; 2. A green oxide containing $V^2O^2.2V^2O^5$; 3. A yellow-green oxide, $V^2O^2.4V^2O^5$; and 4. An orange-yellow oxide. (See Gmelin's *Handbook*, iv. 84.)

The remaining vanadates have not been examined with sufficient exactness to render special description necessary.

VANADIUM, OXYBROMIDE OF, or **VANADYL-BROMIDE**, $VOBr^3$.—This compound (regarded by Schafarik, who discovered it, as tribromide of vanadium, VBr^3), is formed, like the corresponding oxychloride, by igniting a mixture of vanadium-tetroxide and charcoal in bromine-vapour. It forms needle-shaped crystals, having a dark-brown colour and blue metallic iridescence. (Schafarik.)

VANADIUM, OXYCHLORIDES OF.—*a. Vanadium-oxytrichloride*, or *Vanadyl-trichloride*, $VOCl^3$ (usually regarded as vanadium-trichloride), is prepared: (*α*). By the action of chlorine on vanadium-trioxide:

$$3V^2O^3 + 6Cl^2 = V^2O^5 + 4VOCl^3.$$

(*β*.) By burning the dioxide (Berzelius's metal) in chlorine-gas, at a red heat, a greenish-yellow vapour being then formed, which condenses to a liquid.—(γ.) By passing chlorine-gas over an ignited mixture of the trioxide, tetroxide, or pentoxide of vanadium, with charcoal, and condensing the resulting vapours in a cooled U-tube. The liquid is freed from excess of chlorine by passing dry air through it, or by rectifying it over mercury.

Vanadyl-trichloride is a golden-yellow liquid, of specific gravity 1·764 at 20°, (Schafarik), 1·841 at 14·5° (Roscoe). Boiling-point 127°. Vapour-density = 6·41 (Schafarik), 6·108 (Roscoe); calc. (2 vols.) = 6·119. When exposed to the air, it emits cinnabar-coloured vapours, being resolved by the moisture of the air into hydrochloric and vanadic acids. With a small quantity of water, it becomes turbid, from separation of vanadic acid; with a larger quantity, it forms a clear pale-yellow solution, which when left to itself for some time, or more quickly when heated, gives off chlorine, turns green or blue, and then contains vanadium-tetrachloride, or the corresponding oxide, or vanadyl-dichloride. The same effects are produced on dissolving vanadyl-trichloride in hydrochloric acid. The recently prepared solution in hydrochloric acid dissolves gold. Vanadyl-trichloride dissolves also in alcohol, the solution, however, being quickly reduced to a lower chloride. (Schafarik.)

The following experiments show that this compound contains oxygen:—(1.) The vapour, passed over perfectly pure carbon at a red heat, yields carbonic anhydride.—(2.) It oxidises magnesium, converting it into magnesia.—(3.) It converts sodium into caustic soda.—(4.) Its vapour passed, together with hydrogen, through a red-hot tube, yields vanadium-trioxide. (Roscoe.)

β. *Vanadium-oxydichloride*, or *Vanadyl-dichloride*, $VOCl^2$.—This compound, obtained by the action of zinc on vanadyl-trichloride at 400° in sealed tubes, is a light-green crystalline solid, having a specific gravity of 2·88, insoluble in water, deliquescing on long exposure to the air, easily soluble in acids. (Roscoe.)

γ. *Vanadium-oxymonochloride*, or *Vanadyl-monochloride*, $VOCl$, formed by the action of hydrogen upon vanadyl-trichloride at a red heat, is a brown, light, powdery solid, insoluble in water, but easily soluble in acids. (Roscoe.)

δ. *Divanadyl-monochloride*, V^2O^2Cl, is also formed by the action of hydrogen at a red heat. It is easily separated from the preceding compound, as it is a heavy, shining, metallic powder, resembling mosaic gold. (Roscoe.)

VANADIUM, SULPHIDES OF. Two vanadium-sulphides are known, corresponding to the tetroxide and pentoxide.

The *tetrasulphide* or *Vanadious sulphide*, V^2S^4, is produced by heating the tetroxide to redness in a stream of sulphydric acid gas. It is black, very friable, of sp. gr. 4·70, insoluble in water, aqueous alkalis, and sulphides of alkali-metal, not altered by hydrochloric or sulphuric acid, but converted by nitric acid into vanadious sulphate. When heated in the air, it burns, producing sulphurous and vanadic anhydrides.

Hydrated vanadious sulphide is obtained by dissolving a vanadious salt in excess of an alkaline monosulphide, and precipitating with hydrochloric acid. The precipitate is brown at first, but becomes black, without decomposition, on washing and drying.

Vanadious sulphide unites with basic metallic sulphides, forming salts called sulphovanadites. Those of the alkali-metals are obtained by dissolving the hydrated sulphide in monosulphide of ammonium, &c., or by treating a vanadite with excess of sulphydric acid. These sulphosalts are black in the dry state, purple-brown in solution (like the permanganates). The other sulphovanadites are insoluble in water, and are obtained by precipitation. (Berzelius.)

Pentasulphide of Vanadium, or *Vanadic sulphide*, V^2S^5, cannot be formed in the dry way, but is obtained by dissolving the pentoxide, or an alkaline vanadate, in excess of alkaline monosulphide, and precipitating with hydrochloric acid. It is brown when moist, black in the dry state, but yields a brown powder. When heated in a retort, it is resolved in sulphur and the tetrasulphide; by heating in the air, it is oxidised to sulphurous and vanadic anhydrides. It dissolves, with red-brown colour, in aqueous solutions of alkaline carbonates, hydrates, and sulphydrates.

Vanadic sulphide unites with basic metallic sulphides, forming the sulphovanadates. Those of the alkali-metals are soluble in water, and are obtained by dissolving vanadium-pentoxide in excess of alkaline sulphide, or by treating the alkaline vanadates with excess of sulphydric acid; in the dry way also by fusing vanadium-compounds with alkali and sulphur.

The sulphovanadates of alkali-metal are brown in the dry state, red-brown in solution. The aqueous solution of the potassium-salt gives, with alcohol, a scarlet precipitate, which turns brown when washed with alcohol.—The sulphovanadates of barium, calcium, and strontium may be obtained as crystalline powders, slightly soluble in water. All the other sulphovanadates are insoluble in water, and are obtained by precipitation. (Berzelius.)

VANADYL. Syn. with VANADIUM-MONOXIDE (p. 987).

VANADYL-BROMIDE. See VANADIUM, OXYBROMIDE OF (p. 992).

VANADYL-DICHLORIDE. Syn. with VANADIUM-OXYCHLORIDE (p. 993).

VANADYL-TRICHLORIDE. Syn. with VANADIUM-OXYTRICHLORIDE (p. 992).

VANILLA. *Vanille. Vaniglia.*—The fruit of *Vanilla planifolia*, a climbing orchidaceous plant growing wild in Mexico, Brazil, and Guiana, and cultivated in Jamaica, Trinidad, Mauritius, Ceylon, Java, and other tropical countries. The pods, which are nearly cylindrical, five or six inches long, and a line or two thick, have a very pleasant aromatic taste and smell, and are often covered externally with white shining crystals of vanillin, which is their principal constituent. They also contain an iron-greening tannin, a non-drying fat-oil, wax, resin, &c.

Vanilla is used for flavouring ices, creams, chocolate, &c.; also in medicine in the form of powder and of alcoholic tincture.

VANILLIC ACID. Syn. with VANILLIN.

VANILLIN, $C^{10}H^6O^2$ (Gobley); $C^{17}H^{22}O^{15}$ (Stokkebye), the neutral odoriferous principle of vanilla, was formerly mistaken for benzoic, and afterwards for cinnamic acid. It was first recognised as a peculiar substance by Bley (Jahresb. 1858, p. 535; 1859, p. 508), further examined by Gobley (J. Pharm. [3], xxxiv. 401; Jahresb. 1858, p. 534), and afterwards by Stokkebye (Jahresb. 1864, p. 612), who designates it as *vanillic acid*.

Vanillin may be prepared by mixing the alcoholic extract of vanilla with water to a syrupy consistence; agitating with ether, evaporating, and treating the residue with boiling water; again evaporating; and treating the resulting crystals with animal charcoal (Gobley). It crystallises in long, colourless, four-sided prisms, bevelled at the ends. It is nearly insoluble in cold water, moderately soluble in hot water, more easily in alcohol, ether, and volatile oils. The alcoholic solution has a faint acid reaction. It melts at 76° (Gobley), at 82° (Stokkebye), begins to sublime at 150° (Gobley), and distils over with vapour of water (Stokkebye). It dissolves in strong sulphuric acid and in caustic potash. Nitric acid converts it into oxalic acid.

VAPOURS, DENSITY OF. See SPECIFIC GRAVITY (p. 365).

VAPOURS, LATENT HEAT OF. See HEAT (iii. 96).

VAPOUR, TENSION OF. See HEAT (iii. 81).

VAREC. The name applied in Normandy to the ash of seaweed, used as manure and for the preparation of bromine, iodine, and potassium-salts. In Scotland the same substance is called kelp (p. 210).

VARENNA-JUICE. *Succus varennæ.*—The juice of *Varenna polystacha*, a leguminous plant indigenous in Mexico. When dry, it has a brownish vitreous gloss, and consists almost wholly of tannin. (Soubeiran, J. Pharm. [3], xxviii. 196.)

VARIOLARIA. A genus of lichens, several species of which, viz. *V. dealbata*, *V. aspargilla*, *V. orcina*, and others, are used for the preparation of archil.—*V. amara* contains a bitter substance called picrolichenin (iv. 642).

VARIOLARIN. The name applied by Robiquet to a crystalline body, which he obtained from that portion of the alcoholic extract of *Variolaria dealbata* which is insoluble in water. It was probably lecanoric or orsellic acid.

VARIOLITE. A fine-grained to compact diorite, enclosing roundish lumps of felspar.

VARISCITE. A hydrated aluminic phosphate, occurring in quartz and silicious shale at Mosbach in the Saxon Voigtland. It contains small quantities of ferrous oxide, chromic oxide, magnesia, and ammonia, and is apparently related to turquois (iv. 551). It is non-crystalline, has an apple-green colour, and faint waxy lustre; hardness = 5·0 to 5·5. Specific gravity = 2·34 to 2·38. (A. Breithaupt, J. pr. Chem. x. 507.)

VARNISH. *Vernis. Firniss.*—A solution of a resinous substance spread over the surface of wood, metal, &c., and forming shining, transparent, hard crusts, capable of resisting the influence of air and moisture. The principal resins used for making varnishes are copal, animé, mastic, and sandarach; the solvents are spirits of wine, turpentine-oil, or linseed and other drying oils.

Crystal varnish for maps, prints, drawings, &c. is made by dissolving Canada balsam in the best oil of turpentine. (See *Ure's Dictionary of Arts and Manufactures*, iii. 940.)

VARVICITE. A manganese-ore from Warwickshire, consisting, according to Rammelsberg, of $MnO^2.Mn^2O^3.H^2O$; according to Phillips, of $MnO.3Mn^2O^3.H^2O$ (iii. 813).

VASCULOSE. A substance constituting, according to Frémy (Jahresb. 1859, p. 538), the principal part of the vessels of wood. It is distinguished by its insolubility in concentrated acids and in cuprate of ammonia, and is prepared by treating wood, first with dilute potash-ley, then repeatedly with hydrochloric acid, afterwards with cuprate of ammonia, and finally with cold hydric sulphate.

VATERIA. *V. indica*, a tree growing in Malabar, yields a semifluid resin, which hardens in the air, and is used for making Peynie-varnish.

VAUGNERITE. The name given by Fournet (Annal. des Minéral. [4], xix. 149) to a coarse-grained variety of diorite from the gneiss of Vaugneray (Départ. du Rhône), rich in oligoclase, blackish-green hornblende, and brown-black mica.

VAUQUELINE. A name originally given by Pelletier and Caventou to strychnine; also by Pallas to a crystalline substance obtained from the bark of the olive-tree.

VAUQUELINITE. Native chromate of lead and copper. (See CHROMATES, i. 934.)

VEGETABLE ALKALI. Syn. with POTASH (p. 700).

VEGETABLE ETHIOPS. A charcoal prepared by incinerating common seawrack (*Fucus vesiculosus*) in a covered crucible.

VEGETABLE IVORY. This name is applied to the tagua-nut, the fruit of *Phytelephas macrocarpa*, a tree growing on the borders of the Magdalen river in Columbia, South America. It contains about 80 per cent. of woody fibre, is very hard and compact, has the appearance of ivory, and may be turned in the lathe.

VEGETABLE PARCHMENT. See CELLULOSE (i. 819).

VEGETABLES, NUTRITION OF. See NUTRITION OF PLANTS (iv. 162).

VEIN-STONES. *Phlebolites.*—Concretions found in the veins, chiefly of the pelvis, and consisting of calcic phosphate and carbonate, with a small quantity of magnesia, and generally an organic nucleus.

The term *vein-stone* is also applied to the mineral substances which accompany and often enclose metallic ores.

VENETIAN CHALK. Syn. with STEATITE.

VENETIAN RED. A pigment formed of red hæmatite.

VENICE TURPENTINE. See TURPENTINE (p. 919).

VERANTIN. $C^{14}H^{10}O^5$? (Schunck, J. pr. Chem. lix. 474.)—A substance contained in madder-root, whence it is extracted by processes already described (pp. 121, 123). It is a reddish-brown amorphous powder, like snuff or roasted coffee. Boiling water scarcely dissolves it, but renders it soft and coherent. It is easily soluble in boiling alcohol; the solution reddens litmus. It dissolves in alkalis and alkaline carbonates, forming dingy-red solutions, from which it is precipitated in brown flocks by acids. The alcoholic solution forms dark-brown precipitates with cupric and plumbic acetates. Verantin also forms a stannous lake, the preparation of which is described under RUBIAFIN (p. 121). Verantin does not impart any colour to mordanted fabrics.

VERATRIC ACID. $C^9H^{10}O^4$.—An acid existing in sabadilla-seeds; discovered by E. Merck in 1839 (Ann. Ch. Pharm. xix. 180), further examined by Schrötter (*ibid.* xxix. 188), and by W. Merck (*ibid.* cviii. 58). It is prepared by exhausting sabadilla-seeds with alcohol acidulated with sulphuric acid, precipitating the extract with milk of lime, evaporating the filtrate, mixing the clear solution of calcic veratrate thus obtained with sulphuric or hydrochloric acid, and leaving it in a cold place. Veratric acid then crystallises out, and may be purified by solution in alcohol and treatment with animal charcoal.

Veratric acid crystallises from its alcoholic solution by spontaneous evaporation, in slender colourless spiculæ, or four-sided prisms. It has a slight acid reaction; dissolves sparingly in cold, more freely in boiling water; also in alcohol, especially when warm, but is insoluble in ether. At 100° the crystals give off water and become opaque; at a higher temperature they melt to a clear liquid, the acid afterwards subliming without decomposition.

Chlorine and *bromine* act strongly on veratric acid, forming viscid uncrystallisable substitution-products. The acid appears to be but slightly acted upon by *oil of vitriol*, and not at all by *pentachloride of phosphorus*. It dissolves in very strong *nitric acid*, and the solution, when mixed with water, deposits nitroveratric acid, $C^9H^9(NO^2)O^4$, which dissolves easily in alcohol, and crystallises therefrom in small yellow laminæ, melting and decomposing at 100°. This compound, boiled with nitric acid, is converted into dinitroveratric acid, which, however, is difficult to separate from the mononitrated acid. (W. Merck.)

Veratric acid distilled with excess of baryta is resolved into carbonic anhydride and veratrol: $C^9H^{10}O^4 = CO^2 + C^8H^{10}O^2$. (W. Merck.)

Veratric acid is monobasic.—The *veratrates of the alkali-metals* are crystallisable, non-deliquescent, easily soluble in water.—The *lead-salt* is insoluble.—The *silver-salt*, $C^9H^9AgO^4$, is a white precipitate, slightly soluble in water.

Ethylic Veratrate, $C^9H^9(C^2H^5)O^4$, is obtained by passing hydrochloric acid gas into a moderately concentrated solution of veratric acid in strong alcohol, distilling the saturated solution, treating the distillate with water, &c., as a radio-crystalline easily friable mass, having a specific gravity of 1·141 at 18°, inodorous, but having a slightly bitter, burning, and somewhat aromatic taste. It is slightly soluble in water, easily in alcohol, and separates therefrom by spontaneous evaporation in shining needles. It does not volatilise without decomposition; when heated in the air, it burns with a luminous flame. It is decomposed by heating with potash-ley. (Will, Ann. Ch. Pharm. xxxvii. 198.)

VERATRIN. Syn. with VERATRUM-RESIN (p. 997).

VERATRINE. $C^{32}H^{52}N^2O^8$. (Meissner, Neues Journ. v. Trommsdorff, v. 3. —Pelletier and Caventou, Ann. Ch. Phys. [2], xiv. 69.—Couerbe, *ibid.* lii. 352. —Merck, N. Journ. v. Trommsd. xxi. 134.—G. Merck, Ann. Ch. Pharm. xcv. 200.)—An organic base discovered, in 1818, by Meissner, in sabadilla-seeds (p. 141), and soon afterwards by Pelletier and Caventou, in white hellebore (*Veratrum album*); it is probably contained also in other species of veratrum.

Preparation.—1. The evaporated alcoholic extract of sabadilla-seeds is dissolved in dilute sulphuric acid; the solution treated with animal charcoal, and then precipitated by an alkali (100 pts. of the seeds, thus treated, yield 9 pts. veratrine); the precipitate still containing sabadilline and other bodies, is dissolved in dilute sulphuric acid, and nitric acid is added as long as a black pitchy precipitate is thereby produced; the filtrate is precipitated with dilute potash-ley; the washed and dried precipitate is dissolved in absolute alcohol; the solution evaporated; the residue boiled out with water, and the impure veratrine which remains is dissolved in ether, which, on evaporation, leaves the pure base (Couerbe).—2. The pulverised seeds are boiled with water containing hydrochloric acid; the extract is evaporated to a syrup; hydrochloric acid is added as long as it forms a precipitate; the filtered liquid is decomposed with excess of lime; the precipitate is treated with hot alcohol; the extract evaporated; the residue dissolved in dilute acetic acid, and precipitated by ammonia; and the precipitate is purified by ether. By this process, 5 kilogrammes of sabadilla-seeds yield 10 to 15 grammes of veratrine (Merck).—Delondre (J. Pharm. [3], xxvii. 417) prepares pure veratrine by exhausting crushed sabadilla-seeds with water containing hydrochloric acid in a displacement-apparatus, finally washing them with water, precipitating the extracts with a slight excess of potash, and heating the washed and dried precipitate with twice its weight of ether for four hours in a vessel which can be closed. The solution left to evaporate in shallow basins leaves pure veratrine.

Properties.—Veratrine is ordinarily a white or whitish-green crystalline powder; but, by spontaneous evaporation of its alcoholic solution, it is obtained in long prisms with rhombic base (Merck), which effloresce in contact with the air, assuming the aspect of porcelain, and becoming very friable (G. Merck). It is inodorous, but the smallest quantity introduced into the nose produces violent sneezing, accompanied by headache and general uneasiness. It is very acrid and poisonous, producing vomiting and purging when taken internally: 3 milligrammes of it killed a young cat in ten minutes. It is, however, used in medicine as an external application, and when taken internally, in properly regulated doses, is said to exert an antifebrile action. It is insoluble in water and alkaline liquids, very soluble in alcohol, and still more in ether (G. Merck). The solutions turn litmus blue.

Veratrine dried at 100° gives, by analysis, 64·51 to 65·00 per cent. carbon, 8·55 to 8·84 hydrogen, and 5·5 nitrogen (G. Merck). The formula $C^{32}H^{52}N^2O^8$ requires 64·86 C, 8·78 H, 4·73 N, and 21·63 O.

Veratrine melts easily when heated, and decomposes at a higher temperature; but by very careful heating, small quantities of pure veratrine may be sublimed without decomposition.

Strong *sulphuric acid* colours veratrine first yellow, then a fine carmine-red, and ultimately violet; according to Vasmer (Arch. Pharm. ii. 74), 1 pt. of veratrine imparts an amethyst-red colour to 3,000 pts. of the acid.—Strong *nitric acid* is coloured by veratrine, first scarlet, and then yellow.—Strong *hydrochloric acid* dissolves veratrine, especially when heated, forming a deep violet solution, and separating small drops of oily liquid.

Veratrine-salts.—Veratrine dissolves easily in dilute acids, forming colourless salts, which have a sharp burning taste and poisonous action. There appear to be two classes of veratrine-salts, inasmuch as Couerbe obtained crystallisable salts containing 2 at. hydrochloric or 1 at. sulphuric acid to 1 at. veratrine, whereas G. Merck obtained only uncrystallisable gummy salts containing half that proportion of acid.

The solutions of veratrine-salts are inactive to polarised light. Most of them give, with alkaline hydrates, carbonates, and phosphates, precipitates not perceptibly soluble in excess of the reagent. A solution of a veratrine-salt, mixed with tartaric acid, gives a precipitate with acid carbonate of sodium, but not with acid carbonate of potassium. The concentrated solutions give yellow precipitates with auric acid and platinic chloride, yellowish-white with potassium-iodide, light-red with potassium-sulphocyanate, kermes-brown with tincture of iodine, sulphur-yellow with picric acid. Tincture of galls renders the neutral solutions turbid, and on addition of hydrochloric acid, a copious white precipitate is formed.

Chloro-aurate of Veratrine, $C^{32}H^{52}N^2O^8.HCl.AuCl^3$, crystallises from solution in hot alcohol, on cooling, in thin yellow crystals having a silky lustre, and giving, by analysis, 20·87 to 21·26 per cent. gold (calc. = 21·09).

VERATROL. $C^8H^{10}O^2$. (W. Merck, *loc. cit.*)—A compound formed by distilling veratric acid (p. 997), with excess of baryta at a gentle heat. It is a colourless oil, having an agreeable aromatic odour, and specific gravity 1·086 at 15°, solidifying at + 15°, and boiling at 202°—205°.

Veratrol does not appear to unite with alkaline bisulphites. It is not altered by alkalis or by weak acids.—With *potassium* it forms a gelatinous mass without evolution of hydrogen.—*Chlorine* decomposes it, forming at first a crystalline product, converted by the further action of the chlorine into an unctuous mass.

Bromine converts veratrol into dibromoveratrol, $C^8H^8Br^2O^2$, which forms white prismatic crystals, insoluble in water, easily soluble in alcohol and ether, melting at 92°, and volatilising without decomposition at a higher temperature.

Nitric acid acts strongly on veratrol, forming at first nitroveratrol, $C^8H^9(NO^2)O^2$, which crystallises from alcohol in yellow laminæ. By further action of the nitric acid, dinitroveratrol, $C^8H^8(NO^2)^2O^2$, is produced, which forms long yellow needles, sparingly soluble in water, easily in alcohol, melting at 100°, and then volatilising with decomposition.

VERATRUM. *Rad. veratri*, the root of white hellebore (*V. album*), is used in medicine; it contains, according to Pelletier and Caventou, a volatile acid resembling sabadillic acid, also gallic acid and veratrine, together with starch, sugar, and fat; according to Simon, it contains also another base, called jervine (iii. 443).

Veratrum Sabadilla, Retz (*V. officinale*, Schlecht), yields sabadilla-seeds (*Semen sabadillæ*).

VERATRUM-RESIN. *Veratrin.* (Couerbe, Ann. Ch. Phys. [2], lii. 352.)—A constituent of sabadilla-seeds. When the solution decanted from the pitchy precipitate obtained in the preparation of veratrin after treatment with nitric acid (p. 996), is precipitated with potash, and the alcoholic solution of the resulting precipitate is evaporated, there remains a yellow resinous mass; and on exhausting this mass, first with water and then with ether, veratrum-resin remains behind, and may be purified by solution in alcohol and evaporation. This resin is said to have the composition $C^{14}H^{36}N^2O^3$, but it is perhaps only a mixture. It is brown, insoluble in water, ether, and alkalis, melts at 185°, and decomposes at a higher temperature. It unites with acids, but without neutralising them or forming crystalline compounds.

VERBASCUM. The flowers of great mullein (*V. Thapsus*), which are used in medicine as *flores verbasci*, contain, according to Morin, a resinous colouring-matter, volatile and fat oil, together with other constituents; according to Rossignon, the entire plant contains a large quantity of ammonium-nitrate.

VERBENA-OIL, from *Aloysia citriodora*, has a red colour, and yields, by distillation, an oxygenated oil, while the residual resinised portion gives off sulphydric acid when heated (Gladstone, Chem. Soc. J. xvii. 1). Respecting its specific gravity and optical properties, see OILS, VOLATILE (iv. 186).

VERDIGRIS. Basic cupric acetate. See ACETATES OF COPPER (i. 14).

VERDITER. The commercial name of normal cupric acetate, $Cu''(C^2H^3O^2)^2$ (i. 14).

VERMICULITE. A chloritic mineral from Vermont in North America, containing, according to Thomson (*Outlines of Mineralogy*, i. 372), 49·08 per cent. silica, 7·28 alumina, 16·96 magnesia, 16·12 ferrous oxide, and 10·27 water. It resembles scaly talc, but is specially characterised by swelling up very strongly before the blowpipe, and breaking out into vermicular excrescences before it melts. Similar minerals are found at Milbury in Massachusetts and at Westchester in Pennsylvania. (Handw. d. Chem. ix. 214).

VERMILLION. See Mercuric Sulphide (iii. 913).

VERMONTITE. The name of one of the five varieties (poisonous pyrites, mispickel, vermontite, dalarnite, and aconitite) into which A. Breithaupt divides the mineral species, arsenical pyrites, on account of differences in the angles.

VERNONIA. The seed of *V. anthelmintica* is known in commerce as *Calagero.*

VERTIDINE. An organic base, not yet isolated, existing, according to C. Gr. Williams (Chem. Soc. Qu. J. vii. 97), in very small quantity, in the tar of bituminous shale. On separating the volatile bases from the tar by the action of an acid, and subjecting them to fractional distillation, vertidine is found in the portion boiling between 183° and 210°. It imparts a fine green colour to solution of chloride of lime.

VESUVIAN. *Idocrase. Egeran. Gökumite. Loboite. Frugardite. Protheite. Wiluite. Cyprine. Xanthite.*—A calcio-aluminic silicate, $9(2CaO.SiO^2).2(2Al^2O^3.3SiO^2)$, in which the lime is replaced to a small amount by magnesia, ferrous oxide, and manganous oxide, and the alumina to a somewhat greater extent by ferric oxide. For analyses and discussion of formulæ, see Rammelsberg's *Mineralchemie* (pp. 734–739).

Vesuvian occurs in quadratic crystals, usually exhibiting the combination $P \,.\, oP \,.\, \infty P \,.\, P\infty \,.\, \infty P\infty$, &c. [somewhat like *fig.* 322 (Crystallography, ii. 160), supposing the terminal summits very much truncated]. Sometimes crystals occur with a great number of secondary faces. For P, the length of the principal axis is 0·4596. Angle P : P in the terminal edges = 129° 21′; in the lateral edges = 74° 27′. Cleavage indistinct parallel to ∞P and $\infty P\infty$. The crystals usually have the prismatic faces, more rarely the pyramidal faces predominant; they occur implanted and imbedded, intergrown, and forming aggregations of various character, from columnar or fibrous to granular, passing into massive. Fracture conchoïdal or uneven to splintery. Brittle. Hardness = 6 to 7. Specific gravity = 3·2 to 3·5. Colour brown or green, light or dark to nearly black; also yellow, rarely blue. Streak white. Lustre vitreous, sometimes very strong on the crystalline faces; also waxy, especially on the fractured surfaces. Transparent to translucent on the edges only. Before the blowpipe, vesuvian melts easily, and with intumescence, to a yellowish-green or brown glass; with borax or phosphorus-salt it exhibits the iron reaction, and with the latter a skeleton of silica. In its natural state it dissolves but imperfectly in hydrochloric acid; but after fusion it dissolves completely, with separation of gelatinous silica.

Vesuvian was first observed in the ancient Vesuvian lavas; it has since been found in serpentine, gneiss, and granular limestone. The mineral from Vesuvius has a hair-brown or olive-green colour; the crystals from Ala in the Val di Brozzo, in Piedmont, are usually transparent and shining, with a green or brown colour, rarely black. Egg near Christiania in Norway, the Ural, the Wilui river, near Lake Baikal, Cziklowa in the Bannat, and Monzoni in the Fassa valley, are other localities. Sulphur-yellow crystals have been found at Monzoni. A light-brown variety occurs in Donegal, Ireland. The variety called *frugardite* comes from Frugard in Finland; *gökumite*, or *loboite* from Gökum near Dannemora in Sweden. Liver-brown diverging crystals, from Eger in Bohemia, have been called *egeran*. Crystals called *cyprine*, of a blue tint, attributed to copper, come from near Tellemark in Norway; *xanthite* is from near Amity, New York. Vesuvian is found also at many other localities in the United States. (Dana, ii. 199.)

VETCH. See Vicia.

VETIVER. *Kus-kus. Iwarancusa-root.*—The rootstock of an Indian grass, probably *Anatherum muricatum*, and similar species, such as *Andropogon Schænanthus*, &c. It is used in India for making mats, for window-blinds and other coverings, these objects, when moistened with water, exhaling the fragrant odour of the vetiver-root. The root contains two essential oils, the more volatile of which is lighter than water, the other of more viscid consistence. 100 lbs. of root of good quality yield about ⅛ lb. of volatile oil resembling oil of sandalwood.

Citronella-oil, from the leaves of *Andropogon Schænanthus*, consists almost wholly of an oxygenated oil, boiling at 200°, and of specific gravity 0·8741 at 20°. Lemon-grass oil, from *Andropogon Nardus*, is scarcely distinguishable from citronella-oil. (Gladstone, Chem. Soc. J. xvii. 1.)

VIBURNIC ACID. See the next article.

VIBURNUM. A genus of trees and shrubs belonging to the caprifoliaceous order. The bark and berries of the guelder-rose (*V. opulus*) contain valeric acid (viburnic acid). The red berries of the wayfaring-tree (*V. Lantana*), contain, according to Enz (Jahresb. 1863, p. 614), an iron-greening tannic acid, valeric, acetic, and tartaric acids, a bitter principle, an acrid principle, red colouring-matter, sugar, gum, fat-oil, wax, resin, and chlorophyll.

VICIA. *Vetch.*—The seed of the common vetch (*Vicia sativa*) contains the ordinary constituents of leguminous seeds. According to Göbel, 100 pts. of the seeds contain 39 pts. starch and 4 pts. gluten. Greif found 68 pts. starch to 2 pts. gluten, besides sugar, albumin, &c.

The following table exhibits the composition of the ash of three species of vetch. I.—III. Seed of *V. sativa*.—I. according to Sprengel (J. techn. Chem. x. 350).—II. according to Lewi (Ann. Ch. Pharm. l. 421).—III. Vetch from Neufchatel (Cohen, *ibid.* lxxxv. 288).—IV. Straw of *V. sativa*. The air-dried straw contained 10—12 per cent. water, 26·0 substances extractable by water, 30·7 extractable by potash-ley, 42·0 woody fibre, and 5·10 ash (Sprengel, J. techn. Chem. vi. 398).—V. Ash of the entire plant of *V. sativa*. 100 pts. of the fresh plant yielded 82·9 pts. water and 1·1 ash. 1,000 pts. of the dry plant contained 2·38 pts. sulphur (Way and Ogston, Jahresb. 1858, p. 661, Table B).—VI. The tufted vetch (*V. cracca*): the entire plant yielded 68 per cent. water, 11·5 substances soluble in water, 13·8 substances soluble in dilute potash, and 1·626 ash (Sprengel, J. techn. Chem. viii. 355).—7. *Vicia dumetorum* contains, in the flowering state, 68·0 per cent. water, 10·4 substances soluble in water, 11·5 substances soluble in dilute potash-ley, and 2·25 ash (Sprengel, *loc. cit.*):

Ash of Vetches.

	Vicia sativa.					*V. cracca.*	*V. dumetorum.*
	Seed. I.	Seed. II.	Seed. III.	Straw. IV.	Entire plant. V.	Entire plant. VI.	Entire plant. VII.
Quantity of ash . .	2·29	2·40	5·10	2·6	6·50	1·62	2·25
Potash . . .	39·1	30·3	35·5	24·7	32·8	17·6	16·4
Soda	27·1	9·8	. .	13·1	. .	. .	3·0
Lime	7·0	4·7	38·3	8·0	20·7	52·5	55·3
Magnesia . . .	6·2	8·4	6·3	4·8	5·3	8·9	4·3
Ferric oxide . .	0·4	0·7	0·2	0·8	0·6	0·7	
Phosphoric anhydride	6·0	37·8	5·5	29·6	10·6	10·2	7·9
Sulphuric "	2·2	4·1	2·4	9·7	2·5	4·2	5·5
Silica . . .	8·7	2·0	8·7	1·1	1·3	2·9	3·8
Chlorine . . .	1·9	. .	. .	. .	. .	2·2	3·1
Alumina . . .	1·0	. .	0·3				
Manganic oxide . .	0·2	. .	0·1	trace	. .	. .	0·5
Chloride of sodium .	. .	2·0	2·6	7·5	7·3		

According to Schwerz, a hectare yields, on the average, 1,275 kilos. of seed of *Vicia sativa* (15 hectolitres), and 3,000 kilos. straw. The seed contains about 30·6 kilos., the straw 153·1 kilos., the entire plant, therefore, 183·7 kilos. of ash-constituents.

VIGNITE. A mineral from the Jura limestone near Vignes, in the Department of Moselle in France, consisting of greenish-blue grains, bound together by a cement of the same colour but different composition. The grains have a specific gravity of 3·7, and contain, according to Karsten (Archiv. f. Bergbau, xvi. 30), 41·12 per cent. ferric oxide, 29·98 ferrous oxide, 11·87 carbonic anhydride, 3·38 phosphoric anhydride, and 2·9 water, with small quantities of silica, alumina, magnesia, and lime; probably a decomposed iron-ore.

VILLARSITE. A hydrated magnesium-silicate, $4Mg^2SiO^4.H^2O$, with small quantities of iron, manganese, calcium, and potassium, occurring massive, and in granular aggregates, at Traversella in Piedmont. (Dufrênoy, Ann. Min. [4], i. 387.)

VINE. Boussingault (Ann. Ch. Phys. [3], xxx. 389) has determined the quantities of mineral constituents abstracted from the soil by the culture of the vine. As the leaves are returned to the soil, the products actually removed from the vineyard are limited to the wine, the lees, and the branches cut off in pruning. A vineyard of 170 acres, in Alsace, produced, in 1848, 65·05 hectolitres of wine, containing 10·294 kilos. of ash (1·87 grm. per litre); together with 492 kilos. of air-dried lees, containing 6·65 per cent. or 32·72 kilos. of ash; and, finally, 2,624 kilos. of branches, with 2·44 per cent. or 64·03 kilos. of ash. The composition of these ashes was as follows:

Ash of	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3 and Al_2O_3.	SO_3.	Cl_2.	CO_2	P_2O_5.	Sand.	
Wine (1 litre)	0·842	—	0·092	0·172	—	0·096	trace	0·250	0·412	0·006	= 1·870
Lees .	36·9	0·4	10·7	2·2	3·4	5·4	0·4	12·4	10·7	15·3	= 97·8
Branches	18·0	0·2	27·3	6·1	3·8	1·6	0·1	20·3	10·4	10·9	= 98·7

The following table exhibits the quantities of the several mineral constituents removed by the vine-culture from the 170 acres of soil (as calculated from the preceding results,) compared with those removed by other crops grown on equal surfaces of land in the neighbourhood of the vineyard:

Abstracted by	K_2O.	Na_2O.	CaO.	MgO.	P_2O_5.	SO_3.
Wine	11·53	0·13	17·48	3·91	6·66	1·02
Lees	12·07	0·13	3·50	0·72	3·50	1·77
Branches	4·64	. .	0·51	0·95	2·27	0·53
Total . .	28·24	0·26	21·49	5·58	12·43	3·32
Potatoes	107·1		. .	. .	23·8	
Mangold-wurzel . . .	153·0		. .	. .	20·4	
Wheat, with straw . .	45·9		. .	. .	323·0	

Hence it appears that the culture of the vine does not remove more potash from the soil than that of cereals and root-crops.

On the composition of the several parts of the vine, see Crasso (Ann. Ch. Pharm. lvii. 69; lxii. 59; Jahresb. 1847–1848, p. 1082; Table B. Nos. 45–53).—On the ash of the several parts, also Berthier (Ann. Ch. Phys. [3], xxxiii. 249; Jahresb. 1851, p. 708).

In the juice exuding in spring from fresh-cut surfaces of the vine, Wittstein (Jahresb. 1857, p. 520), found chiefly potash, combined with citric and lactic acids; malic acid was not present.

VINETIN (from *vinetier*, the French name of *Berberis vulgaris*). The name given by Wacker to the base obtained by Polex from the root-bark of the common barberry, and by him called oxyacanthin (iv. 288). This latter name has also been given by Leroy to another base extracted from the white thorn (*Cratægus oxyacantha*).

VINEGAR. See Acetic Acid (i. 7).

VIOLA. The fragrant flowers of the violet (*V. odorata*) are said to contain, besides colouring-matter, slight traces of a volatile oil, two acids, one red and the other colourless, an emetic principle called violin (probably identical with emetin from ipecacuanha-root) (ii. 485), sugar, and other substances. The colouring-matter of the flowers is easily turned red by acids, and green by alkalis. The colourless acid called violenic acid by Peretti (Buchn. Repert. xl. 130), is said to crystallise in silky needles, to be soluble in water, alcohol, and ether, and to form yellow salts which stain the skin.

Viola tricolor (heartsease or pansy) contains a yellow colouring-matter, resin, vegetable mucus, and other substances, but no violin. (Boullay.)

VIOLA-EMETIN. Syn. with Violin (p. 1001).

VIOLAN. A silicate of aluminium, calcium, magnesium, and sodium, containing also iron and manganese, from St. Marcel in Piedmont. It occurs massive, and in indistinct, elongated, granular concretions, cleavable in two directions inclined at nearly 90°. It is nearly opaque, with a dark violet-blue colour, and vitreous lustre; hardness = 5 to 6; specific gravity = 3·233. (Plattner, J. pr. Chem. xv. 329.)

VIOLANTIN. $C^8N^6H^6O^9$. (Baeyer, Ann. Ch. Pharm. cxxvii. 223.)—A compound containing the elements of violuric and dilituric acids, and produced by their direct combination, just as alloxantin is formed from alloxan and dialuric acid:

$$\underset{\text{Violuric acid.}}{C^4N^3H^3O^4} + \underset{\text{Dilituric acid.}}{C^4N^3H^3O^5} = \underset{\text{Violantin.}}{C^8N^6H^6O^9}.$$

A mixture of the hot concentrated solutions of the two acids deposits violantin on cooling, in crystals containing $C^8N^6H^6O^9.4H^2O$. Violantin is likewise always produced by imperfect oxidation of violuric acid, or by imperfect reduction of dilituric acid. It may also be prepared by gently heating hydurilic acid with dilute nitric acid (the vessel being dipped into hot water), till a yellow colouring appears on the edges; on removing it, a brisk reaction sets in, and violantin separates as a yellowish-white crystalline body. If too little heat has been applied, the product is chiefly violuric acid; if, on the other hand, the mixture has been too strongly heated, dilituric acid is the principal product.

Violantin dissolves in *water*, but is resolved at the same time into violuric and dilituric acids. The same decomposition takes place on heating it with solutions of salts of the stronger acids, a diliturate of the base being then separated, and violuric acid remaining in solution. On heating it with *acetates*, both diliturate and violurate of the base are produced, the less soluble diliturate separating out, but in most cases strongly coloured by adhering violurate. From a mixture of equal parts of alcohol and water, violantin may be partly crystallised without decomposition.—*Ammonia-gas* colours violantin blue; aqueous ammonia decomposes it into violurate and diliturate.—*Sulphydric* and *hydriodic acid* easily reduce violantin to uramil.

Dry violantin heated to 120°, decomposes immediately through the entire mass, giving off gas, and leaving a brown substance which dissolves with red colour in caustic potash.

VIOLENIC ACID. See VIOLA (p. 1000).

VIOLET (ANILINE). *Hofmann's violet* consists of triethylrosaniline (iv. 471). According to Duprey (Bull. Soc. Chim. 1867, i. 95), it may be rendered soluble in water by decomposing the hydriodate with boiling caustic soda, and redissolving in an acid. Poirrier and Chappat (*ibid.* 1866, ii. 502) describe methods of preparing violet dyes from methyl-, ethyl-, and amyl-aniline, without first preparing rosaniline. Lauth (*ibid.* 362) prepares methylaniline-violet by simply heating certain salts of methylaniline. Thus, when a mixture of 10 pts. methylaniline, 3 pts. hydrochloric acid, and 200 pts. sand, is heated to 100°—220°, and the crude product exhausted with water, a solution is obtained having a very deep and pure violet colour. The colouring-matter contained in it may be purified from a trace of tarry matter, by precipitating with an alkali or alkaline salt, and redissolving the precipitate in water. A second precipitation yields the methylaniline-violet quite pure, and in the form of a fine green mass, which constitutes the commercial product. A similar product is obtained by subjecting methylaniline to the action of powerful oxidising agents, such as cupric nitrate, mercuric acetate, &c.

VIOLIN, or **VIOLA-EMETIN.** An emetic substance contained, according to Boullay, in all parts of the common violet. It has not been obtained pure, and is, perhaps, identical with emetin from ipecacuanha-root.

VIOLINE. This name was given by Price (Rep. of Patent Inventions, Feb. 1860), to a blue precipitate obtained by treating aniline with sulphuric acid and peroxide of lead.

VIOLURIC ACID, $C^4N^3H^3O^4$, or *Nitrosobarbituric acid*, $C^4N^2H^3(NO)^2O^3$. (Baeyer, Ann. Ch. Pharm. cxxvii. 200.)—An acid produced:—1. By the action of nitric acid, nitrous acid, or a metallic nitrite on hydurilic acid:

$$\underset{\text{Hydurilic acid.}}{C^8N^4H^6O^6} + HNO^3 = \underset{\text{Violuric acid.}}{C^4N^3H^3O^4} + \underset{\text{Alloxan.}}{C^4N^2H^2O^4} + H^2O.$$

$$\underset{\text{Hydurilic acid.}}{C^8N^4H^6O^6} + KNO^2 + 2HNO^2 = \underset{\text{Violurate of potassium.}}{C^4N^3H^2KO^4} + \underset{\text{Alloxan.}}{C^4N^2H^2O^4} + 2H^2O + N^2O^2.$$

2. Together with other substances, by the partial reduction of dilituric acid, ($C^4N^3H^3O^5$), as when that compound is cautiously heated with glycerin, or when ferrous diliturate is reduced by solution of potassium-cyanide.

To prepare it, hydurilic acid is warmed with water and nitrate of potassium, whereby deep-blue violurate of potassium is formed, the quantity of which may be increased by alternately adding small quantities of acetic acid (to neutralise free potash, which would exert a decomposing action) and nitrate of potassium. After filtering off the mother-liquor, the violurate of potassium is washed with a small quantity of water, mixed in hot solution with chloride of barium, and the precipitated violurate of barium is exactly decomposed by dilute sulphuric acid. The filtrate evaporated at 60°—70°, yields pure violuric acid (about ⅗ of the hydurilic acid used).

Violuric acid crystallises in shining, yellowish, rhombic octahedrons, containing $C^4N^3H^3O^4.H^2O$. They give off their water of crystallisation at 100°, dissolve with moderate facility in cold, more easily in hot water; the solution is not precipitated by alcohol.

Violuric acid soon turns mouldy in aqueous solution, and decomposes at the boiling heat; the dry acid likewise decomposes when strongly heated, giving off red fumes.—*Nitric acid* converts it into dilituric (nitrobarbituric) acid.—*Bromine* converts it, in aqueous solution, into alloxan-bromide or dibromobarbituric acid, and hydrobromic acid, with evolution of red vapours:

$$\underset{\text{Violuric acid.}}{2C^4N^2H^3(NO)O^3} + 4Br^2 + H^2O = \underset{\text{Dibromobarbituric acid.}}{2C^4N^2H^2Br^2O^3} + 4HBr + N^2O^3.$$

Heated with *chloride of lime*, it yields chloropicrin.—Heated with *caustic potash-ley*, it gives off a small quantity of ammonia, and is converted into hydrovioluric acid, a compound not yet examined.—Violuric acid heated with *soda-lime*, gives off all its nitrogen in the form of ammonia.

Reducing agents, such as *sulphydric, hydriodic acid*, &c., convert violuric acid into uramil (amidobarbituric acid):

$$\underset{\text{Violuric acid.}}{C^4N^2H^3(NO)O^3} + 2H^2S = \underset{\text{Uramil.}}{C^4N^2H^3(NH^2)O^3} + S^2 + H^2O.$$

With *sulphite of ammonium*, it forms sulphuric acid and thionurate of ammonium.—With *dilituric acid* it unites directly, forming violantin.

Violurates.—Violuric acid is monobasic. It decomposes acetates, but not chlorides. Its salts are distinguished by the great beauty and variety of their colours.

Violurate of Ammonium, $C^4N^3H^2(NH^4)O^4$, crystallises in fine, dark-blue, anhydrous prisms.—The *potassium-salt*, $C^4N^3H^2KO^4.2H^2O$, forms deep-blue laminæ or prisms, which dissolve in hot more easily than in cold water, forming a deep-blue solution. At 115°—120°, the salt gives off its water, and becomes greenish-blue. The solution mixed with excess of potash, turns red, perhaps from formation of a basic salt. A solution of potassium-violurate in hot concentrated hydrochloric acid deposits, on cooling, the compound $2(KCl.C^4N^3H^3O^4).HCl.6H^2O$, in large, colourless, shining, efflorescent prisms, easily soluble in water, sparingly in alcohol. At 100°, these crystals give off water and hydrochloric acid, leaving the compound $KCl.C^4N^3H^3O^4$.—*Violurate of sodium* forms red nodules composed of short needles, easily soluble in hot water.

Violurate of barium, $C^8N^6H^4Ba''O^8.4H^2O$, is precipitated by chloride of barium from a solution of the potassium-salt, in red shining quadratic tables, which are nearly insoluble in cold water, and give off all their water of crystallisation at about 230°.—The *calcium-salt* forms brick-red crystals.—The *cupric salt* is an amorphous olive-green precipitate.—*Ferrous salt.* Violuric acid added to ferrous acetate forms a dark-blue solution, from which alcohol precipitates ferrous violurate in six-sided tables with red metallic lustre; they dissolve easily in water, forming a dark-blue solution.—The *lead-salt*, $C^8H^4Pb''N^6O^8.4H^2O$, is obtained, by double decomposition, in small red crystals, becoming dark-red when dry. A reddish basic salt (containing 68 per cent. lead, and 0·5 hydrogen), is formed by precipitating the potassium-salt with basic acetate of lead.—The *magnesium-salt*, $C^8H^4Mg''N^6O^8.6H^2O$, separates, on cooling, from a warm mixture of magnesium-acetate and violuric acid or the potassium-salt, in hard, shining, purple-red, rhombic cystals, becoming dark-red when dry.—The *silver-salt* is a violet gelatinous precipitate.

VIRGINIA CREEPER. *Ampelopsis hederacea. Vitis hederacea*, L. *Hedera quinquifoliæ*, Du Roi.—The leaves of this plant, which turn red in autumn, contain a red colouring-matter, called by Wittstein cissotannic acid, which may be extracted by alcohol. 100 pts. of the fresh leaves yielded 1·56 per cent. ash, containing in 100 pts.: 23·9 K^2O, 12·0 Na^2O, 20·2 CaO, 8·0 MgO, 0·1 Al^2O^3, 0·6 Fe^2O^3, 3·1 SO^3, 15·1 P^2O^5, 5·0 SiO^2, 10·0 CO^2, and 1·8 Cl (Wittstein, Buchn. Repert. xcvi. 318).—The berries contain malic, tartaric, and citric acids (Riegel, Arch. Pharm. [2], lv. 153.)

VIRGINIC ACID. An acid obtained, according to Quevenne (J. Pharm. xxii. 449), by heating the fat-oil of the Virginian senega-root to 200°. It is described as a reddish-yellow oil, having a strong odour and sharp taste, soluble in alcohol, ether, and alkalis.

VIRIDE ÆRIS. Syn. with VERDIGRIS.

VIRIDIC ACID. $C^{14}H^{14}O^8$ (?) (Rochleder, Ann. Ch. Pharm. lxiii. 193.)—An acid produced by the oxidation of caffetannic acid in presence of ammonia. Coffee-beans owe their green colour to a small quantity of calcic viridate. To prepare the acid, the solution obtained by decomposing caffetannate of lead (i. 709) with sulphydric acid is supersaturated with ammonia, and left in contact with the air for thirty-six hours, till it acquires a deep-blue colour; then mixed with excess of acetic acid, which colours it brown; then with alcohol, which precipitates a few black flocks (of ulmous substance). The liquid filtered from these flocks is precipitated with acetate of lead, and the blue precipitate of lead-viridate is decomposed by sulphydric acid. The brown solution thereby obtained leaves viridic acid, on evaporation, as an amorphous mass of the same colour, and very soluble in water. The solution forms a blue precipitate with acetate of lead, greenish-blue with baryta-water, and is instantly coloured deep-green by ammonia, potash, or soda. Viridic acid dissolves in strong sulphuric acid, forming a solution of a fine crimson colour, from which water throws down a blue flocculent precipitate.

VIRIDIN. Syn with CHLOROPHYLL.

VIRIDINE. $C^{12}H^{19}N$.—A base obtained from coal-tar. Specific gravity = 1·017. Boiling-point 230°. Slightly soluble in water, easily in alcohol and ether.—The *platinum-salt*, $2(C^{12}H^{19}N.HCl)PtCl^4$, is greenish-brown, insoluble in alcohol and in ether.—The *mercuric salt* crystallises from water, and melts at 35°. (Thenius, Jahresb. 1861, p. 503.)

VIROLA TALLOW. The fat of *Virola sebifera*, Aubl. (*Myristica sebifera*, L.), a tree indigenous in Carolina and Guiana. It is obtained by boiling the shelled and bruised almonds with water; has a yellowish colour, melts at 40°—50°, dissolves in alcohol and ether, partly also in ammonia, and is slowly but completely saponified by potash. (Bonastre, J. Pharm. xix. 186.)

VISCAUTSCHIN. The portion of crude viscin which is insoluble in alcohol and ether, and, according to Reinsch, forms the chief constituent of bird-lime (i. 589).

VISCENE. An oil obtained by the dry distillation of viscin.

VISCIC ACID. See the next article.

VISCIN. A substance which forms the glutinous constituent of the stalks, leaves, and especially the berries of the mistletoe (*Viscum album*), and is the principal constituent of bird-lime. It is also contained in the receptacle and floral envelopes of *Atractylis gummifera* (Macaire, J. pr. Chem. i. 415); in the bark of the holly (*Ilex aquifolium*) (Bouillon-Lagrange); in the milky juice of *Ficus religiosa* (Nees v. Esenbeck), and in the glutinous substance which coats the branches of *Robinia viscosa*. (Vauquelin.)

Crude viscin is obtained by bruising the finely-scraped bark of the mistletoe, and kneading it with water as long as anything is thereby dissolved. A yellow, very viscid, and glutinous mass then remains, containing (besides woody fibre, part of which may be mechanically removed), pure viscin, a waxy substance soluble in alcohol, and a mass insoluble in alcohol and ether, called viscautschin. To obtain pure viscin, the crude mass is boiled several times with strong alcohol; the undissolved portion macerated five or six times with ether, at ordinary temperatures, for twelve hours; and the residue left on evaporating the ethereal extracts is kneaded first with alcohol, as long as this solvent takes up anything, and then with water. (Reinsch, Jahresb. 1860, p. 541.)

Viscin thus obtained is clear, colourless, nearly inodorous, and tasteless; has the consistence of honey at ordinary temperatures; may be drawn out into very fine threads; has the same density as water; becomes more fluid at 30°, and at 100° is as fluid as oil of almonds, and makes a greasy stain on paper. It has an acid reaction. (Reinsch.)

Viscin is decomposed by dry distillation (the boiling-point rising from 210° to above 275°), a mobile oil called viscene first passing over, then a greenish oil, and afterwards a crystalline buttery mass, while a black substance resembling asphalt remains in the retort.

Viscene is a very mobile yellowish oil, of specific gravity 0·85, and distilling almost completely at 226°. When mixed with soda-ley, it solidifies to a crystalline pulp, which, when distilled with water, gives off a fragrant oil called viscinol, while the remaining impure sodium-salt contains an acid called viscic acid, which, in the free state, is an oil having a strong acid reaction, and a faint odour like that of angelic acid. (Reinsch.)

Viscautschin is contained in the portion of crude viscin which is insoluble in alcohol and ether. To purify it, the residue is repeatedly treated with rectified oil of turpentine, which leaves woody fibre undissolved; the solution is mixed with water, and evaporated; the clear yellowish residue is treated with ether, in which it now dissolves; the ether is evaporated; and the residue is repeatedly washed with alcohol, and dried at 100°.

Viscautschin has a density of 0·978. It is extremely viscid and glutinous, being, in fact, the substance to which bird-lime owes its adhesive properties. At 120° it has the consistence of olive-oil. Crude viscin contains about 0·5 pt. viscin, 0·2 viscautschin, and 0·3 waxy matter. (Reinsch.)

VISCINOL. See the last article.

VISCOSIMETER. This name is given by Dollfus to an apparatus for measuring the viscosity of colouring liquids thickened with gum, &c., by comparing the time required by a given quantity of the liquid to pass through a certain aperture, with that required by an equal quantity of water.

VISCUM. The leaves and younger branches of the mistletoe (*Viscum album*) contain (according to Winckler), besides viscin, about 16·7 per cent. uncrystallisable sugar, 5·8 fat-oil, together with tannin, gum, &c., and a small quantity of a volatile odoriferous principle.

The ash of the leaves and branches contains, according to Fresenius and Will, and according to Reuling, the constituents given under *a* in the following table. C. Erdmann found in the leaves, 62·5 per cent. water and 3·85 ash, containing the constituents given under *b*; in the stalks of a mistletoe growing on an apple-tree he found 56·68 per cent. water and 1·9 ash, composed as under *c*. Reinsch found the ash of the stalks and leaves of a mistletoe growing on a Scotch fir, to contain, in 100 pts., the constituents given under *d*. The bark of the stem contains white viscin, gum, sugar, albumin, tannic acid, pectin, and similar substances (Reinsch); the ripe fruit contains resinous substances (bird-lime), gum, wax, &c.:—

Ash of Mistletoe.

	K^2O.	Na^2O.	CaO.	MgO.	$Fe'''Pb^4$.	P^2O^5.	SO^3.	CO^2.	SO^3.	Cl.	NaCl.
a.	35·3	. .	19·4	19·5	1·8	16·6	1·4	13·1	1·6	. .	1·0
b.	19·7	4·3	22·6	9·3	1·6	16·4	2·0	16·8	1·2	0·8	
c.	20·1	4·1	22·2	9·7	1·6	16·3	2·0	15·7	1·0	0·8	
d.	22·0	3·8	21·7	11·7	6·5	14·1	1·7	15·8	1·7	0·6	

VITELLIN. This name was given to the albuminoïdal substance of the yolk of birds' eggs, now known to be merely a mixture of albumin and casein.

VITEX. The seed of *Vitex Agnus castus* is said to contain a peculiar bitter principle called **castine** (i. 814), a volatile acrid substance, a large quantity of free acid, and fat-oil. In Greece, the fresh and rather unripe berries are said to be added to the must of the grape, to render the wine more intoxicating, and prevent it from turning sour. (Landerer, Buchn. Repert. liv. 20; lxxxi. 229; Buchn. N. Repert. iii. 392.)

VITIS. See VINE and VIRGINIA CREEPER (pp. 999 and 1002).

VITRINOPAL. *Vitrite.*—The matrix of Bohemian pyrope, related to pitchstone, and containing, according to Wertheim, 83·72 per cent. silica, 3·58 ferric oxide, 7·57 lime, 0·67 magnesia, and 11·46 water. (Handw. d. Chem. ix. 288.)

VITRIOL. An old name for sulphates, still frequently used in commercial language, the several vitriols being distinguished by their colours, or by the metals which they contain: *e.g.*, white or zinc-vitriol, blue or copper-vitriol, red or cobalt-vitriol, green or iron-vitriol, lead-vitriol, nickel-vitriol, &c. Ferroso-cupric sulphates, obtained in the preparation of cupric sulphate on the large scale from ferruginous materials, are known as Admont, Bayreuth, and Salzburg vitriols (p. 593).

VITRIOL, OIL OF. Concentrated sulphuric acid.

VITRIOL-OCHRE (the *Pitticite* of Beudant) is a basic ferric sulphate found in the copper-mines of Fahlun in Sweden. It contains 15·9 per cent. SO^3, 62·4 Fe^2O^3, and 21·7 water = $2Fe^2O^3.SO^3.6H^2O$.

VITRITE. Syn. with VITRINOPAL.

VITRUM ANTIMONII. An oxysulphide of antimony, formed by fusing tetroxide of antimony with sulphur (i. 328).

VIVIANITE. Native ferrous phosphate. (See PHOSPHATES, iv. 564.)

VÖLCKNERITE. See HYDROTALCITE (iii. 219).

VOGLITE. A carbonate of uranium, copper, and calcium, occurring at Joachimsthal in Bohemia. (See CARBONATES, i. 798.)

VOIGTITE. A micaceous or chloritic mineral, occurring in the graphic granite of Ehrenberg, near Ilmenau, in the Thuringian Forest, forming green soft laminæ, mostly turned brown by weathering. Specific gravity = 2·91. It gives off water when heated, and before the blowpipe, exfoliates strongly, turns dark-brown, melts easily to a black glass, and gives with fluxes the reactions of iron. It is easily decomposed by hydrochloric acid, forming a yellow solution, with separation of tumefied silica. According to Schmid (Pogg. Ann. xcvii. 108), it contains 33·02 per cent. silica, 13·08 alumina, 33·15 ferric oxide, 7·28 magnesia, 1·99 lime, ·96 soda, and 9·52 water.

VOLBORTHITE. Calcio-cupric vanadate. (See VANADIUM, p. 991.)

VOLCANIC GLASS. Syn. with OBSIDIAN (iv. 169).

VOLCANITE. Selenide of sulphur, from Vulcano, one of the Lipari Islands.

VOLGERITE. Antimonic hydrate, $5H^2O.Sb^2O^5$, or $Sb''H^3O^5$, occurring as a white powder or crust with cervantite (i. 524), and resulting from its alteration.

VOLTAGOMETER. A peculiar rheostat or current-regulator, invented by Jacobi. (Pogg. Ann. lxxviii. 173).

VOLTAIC ELECTRICITY. See ELECTRICITY (ii. 414).

VOLTAITE. A ferroso-ferric sulphate, containing alumina, occurring at the Solfatara, near Naples, in opaque octahedrons and other monometric forms, having a resinous lustre, dull green brown or black colour, and greyish-green streak. According to Abich (Berg. u. hütt. Zeitung, 1842, No. 17), it contains 48·32 per cent. SO^3, 2·20 Al^2O^3, 17·65 Fe^2O^3, 11·6 FeO, 4·04 K^2O, 6·25 Na^2O, and 15·94 water, whence Rammelsberg deduces the formula $3(\frac{4}{5}Fe''.\frac{1}{5}K^2)SO^4.2(\frac{5}{6}Fe.\frac{1}{6}Al)'''(SO^4)^3.12H^2O$.—A similar mineral, containing manganous as well as ferrous oxide, has been found by Ulrich at the Rammelsberg mine, near Goslar in the Harz.

VOLTAMETER. An apparatus for measuring the force of an electric current by the quantities of hydrogen and oxygen evolved in the electrolysis of water. (See ELECTRICITY, ii. 433.)

VOLTZIN or **VOLTZITE.** An oxysulphide of zinc, Zn^5S^4O, occurring in implanted spherical globules at Rosières in Puy-de-Dome, and at the Elias mine near Joachimsthal in Bohemia. Hardness = 4·5. Specific gravity = 3·66. (Fournet, Ann. Ch. Phys. [2], xli. 426.—Landecker, Jahrb. geol. Reichsanstalt, iv. 120.)

VOLUME. The volume of a regularly-formed body may be calculated from measurements of its linear and angular dimensions. The volume of an irregular body may be found from its weight and specific gravity—that is to say, the weight of a unit-volume. If w be the weight of the body in grammes, and s its specific gravity, the fraction $\frac{w}{s}$ gives its volume in cubic centimetres.

The capacities of vessels are determined by filling them with water or mercury from a measuring tube or other vessel, whose capacity is previously known, or, when very great accuracy is required, by determining the weight of water or mercury at the standard temperature which fills the vessel. The capacities of wooden vessels may be estimated with sufficient accuracy, for commercial purposes, by filling them with measured quantities of sand or fine-grained seeds, taking care to shake the vessel from time to time, so that the grains may lie close together.

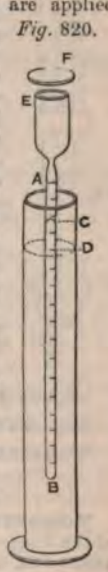
The volume of a large cavity, or vessel full of water, might in some cases be conveniently determined by dissolving a known weight of a soluble substance in the water, say 1 kilogramme of common salt, agitating the water to secure uniformity, and then analysing one litre of it. If this litre were found in the above case to contain one gramme of salt, it would be apparent that the cavity or vessel contained 1,000 litres of water.

VOLUME, ATOMIC or **SPECIFIC.** (See ATOMIC VOLUME, i. 440.)

VOLUMENOMETER, or **STEREOMETER.** These names are applied to instruments for measuring the volume of a solid body by the quantity of a liquid or of air which it displaces, and thence also determining its specific gravity. A very simple apparatus of this kind was used by Playfair and Joule in their experiments on atomic volumes (Chem. Soc. Mem. ii. 477). It consists of a globular flask provided with a narrow neck, about twelve inches long, and graduated from below upwards to indicate grains of water. The flask has a tubulure, accurately fitted with a ground stopper, for admitting the solid body to be measured. The instrument being filled to the mark 0° on the neck with water, oil of turpentine, or other liquid which does not act upon the solid, it is inclined on one side, the stopper removed, and the solid body carefully introduced. The stopper is then replaced, and the number of divisions through which the liquid is raised in the stem gives at once the volume of the body in grain-measures. Any other unit of graduation might of course be adopted.

The stereometer, invented by Captain M. K. Say, of the French Engineers, for determining the specific gravity of gunpowder, is an instrument which measures the volume of a body by the amount of air which it displaces.

Fig. 820.



The simplest form of this instrument is shown in *fig.* 820, where AB is a uniform graduated glass tube, open at the bottom, and communicating by a small hole with the glass vessel AE, which can be closed air-tight, by a piece of ground plate-glass, F. The instrument is immersed in a cylindrical glass vessel, full of clean mercury. If, now, AB be plunged into the mercury up to A, the zero of the scale, and the upper end of the vessel AC be then closed air-tight, we may, by again raising the tube, diminish the pressure on the air within by the weight of a measurable column of mercury; we also learn the increase of the volume of the air, provided we know the capacity of the divisions of the tube AB, which we shall suppose known. Thus suppose that, on the tube being raised, the mercury within stands at C, and without at D, then h being the ordinary barometric pressure of the atmosphere at the time, $h - \mathrm{CD}$ (inches) is now the pressure on the air within. If u be the capacity of the vessel AE, down to the zero A, we find that—

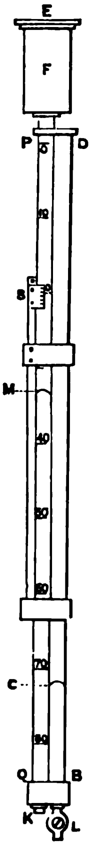
Under the pressure h, the air within has the volume u;
" " $h - \mathrm{CD}$ " " $u + \mathrm{vol.\ AC}$.

Hence, by the law that the volumes of gases are inversely as their pressures, we find—

$$\frac{u}{u + \mathrm{vol.\ AC}} = \frac{h - \mathrm{CD}}{h}, \text{ or } u = \frac{h - \mathrm{CD}}{\mathrm{CD}} \mathrm{vol.\ AC}.$$

Now, if we place any object, as sand, gunpowder, a soluble salt, &c., having the total volume v, in the vessel AC, we may proceed, as before, to find the volume $u - v$ of air still remaining in AE; and as u is already known, we thus find v, in cubic inches. From the volume v, the weight of the objects in AE, and the weight of a cubic inch of pure water at 60°, we may, by a simple calculation, find the specific gravity of the objects.

Fig. 821.



The stereometer has been rendered much more accurate and convenient by Prof. W. H. Miller, whose form of the instrument, as employed by him in finding the specific gravity of standard weights not allowed to be weighed in water, we will now describe, referring to the Phil. Mag. [1834] v. 203, and Phil. Trans. [1856] cxlvi. 799.

It consists of two glass tubes, PQ, DB (*fig.* 821), of equal diameter, communicating with each other at their lower ends, which are cemented into the oblong piece of iron, QB. Below the ends of the tubes are holes concentric with the tubes, that below PQ being closed by the screw K, while below DB is the stopcock L. On the upper end of PQ is the metallic cup F, which may be closed air-tight by the plate of glass E, smeared with lard. The tube PQ is accurately marked with a scale of centimetres, and the fractional parts of the divisions may be read off by the ivory scale S, a centimetre long, divided to every fifth of a millimetre. Some contrivances of Prof. Miller for avoiding error of parallax in this reading need not here be described.

To use this instrument, the object experimented on is placed in a cup within the vessel F; and mercury is poured into the tube at D, until both tubes are nearly full, and the surface in PQ stands exactly at zero of the scale. The plate E is now placed air-tight upon F, which being accomplished, the stopcock E is opened, and mercury is allowed to run out, until the difference of altitude of the mercury in the two tubes is nearly equal to half the height of the barometer at the time. Suppose the mercury in PR now to stand at the point M, and in DB at the point C; then the pressure within F is less than the atmospheric pressure by the weight of the column of mercury, MC, which corresponds to the column of mercury, CD, in the simple form of instrument above described (*fig.* 820). Hence, by the formula already given, we may find the volume of air within F, occupied or unoccupied by other objects. This is on the condition, however, that we know the volume PM, and it is necessary to determine accurately the capacity of the divisions of the tube PQ by the usual method of filling it with mercury, and weighing the portions as they run out, corresponding to given lengths of the tube. To facilitate this operation, F may be unscrewed, and the stopcock L substituted; and the instrument being inverted, mercury may be poured in through a tube-funnel at the opening K.

The results of this instrument are much affected by changes of temperature, and will be uncertain and inexact, except in the hands of a skilful and careful operator. Actual readings of a good barometer at the time are also necessary. (See Barometer, i. 509.) W. S. J.

VOLZIN and **VOLZITE.** Syn. with Voltzin and Voltzite.

VORAULITE. Syn. with Lazulite (iii. 477).

VORHAUSERITE. A massive dark-brown variety of serpentine from Monzoni in the Flemser valley, Tyrol: specific gravity = 2·45. (Oellacher, Jahrb. geol. Reichsanstalt, 1857, p. 258.)

VOSGITE. This name was given by Delesse to a green felspar from the porphyry of the Vosges, and from the gabbro of Mont Genèvre. Rammelsberg has, however, shown that it is merely a decomposed labradorite.

VULCANISATION. The process of combining caoutchouc with sulphur, at high temperature, whereby it acquires increased elasticity (i. 739). Oils heated with sulphur likewise form more or less tenacious and elastic masses; and Perra has shown (Compt. rend. xlvii. 878), that linseed-oil heated with chloride of sulphur yields a product of this nature, which he calls vulcanised oil. 100 pts. linseed-oil heated with 25 pts. chloride of sulphur (saturated with sulphur), yield a product of considerable hardness, though not so hard as ebonite. It is opaque, brittle when cold, permanent in the air; withstands the action of dilute mineral acids and alkalis, but is decomposed by them in the concentrated state; turns brown at 120°, and decomposes at a somewhat higher temperature; becomes strongly electric by friction.

VULCANITE, or **EBONITE.** Hardened caoutchouc.

VULPIC ACID. $C^{19}H^{14}O^5$.—An acid occurring in *Cetraria vulpina* (*Lichen vulpinus*, L.), a lichen which grows in Norway, and is there collected for mixing with nux vomica, as poison for wolves. It was first separated by Bebert (Ann. Ch. Pharm. ii. 342),—who called it vulpulin,—but in an impure state, so that it was regarded by Berzelius as identical with the colouring-matter of *Parmelia parietina*, and was afterwards mistaken for chrysophanic acid, till its true composition was demonstrated by Strecker and Möller (*ibid.* cxiii. 56), who designated it vulpic acid. It is very much like usnic acid (p. 570), from which it differs only by the elements of 2 at. water.

To prepare vulpic acid, the lichen is macerated with 20 pts. of lukewarm water, and a little milk of lime for six hours, and then strained; the residue is again exhausted with 10 pts. of warm water; the united extracts are slightly supersaturated with hydrochloric acid; and the yellow flocculent precipitate, consisting of vulpic acid contaminated with resin and chlorophyll, is purified by recrystallisation from strong boiling spirit or from ether. 100 pts. of the lichen yield about 12 pts. of the acid.

Vulpic acid separates from its ethereal solution on cooling, in transparent yellow needles; by slow evaporation it is obtained in well-defined, bulky, transparent, monoclinic crystals, having nearly the colour of rhombic sulphur. It is nearly insoluble in *water* even at the boiling heat, dissolves with difficulty also in boiling absolute *alcohol*, and separates for the most part on cooling; more easily in *ether*, but most abundantly in *chloroform*, which might therefore be advantageously used for extracting it from the lichen. It melts at a temperature above 100°, and solidifies in the crystalline form on cooling. At a stronger heat it decomposes, leaving a small quantity of charcoal, and giving off a yellow smoke, which condenses partly in brown drops, partly as a yellow powder.

Vulpic acid boiled with excess of *potash-ley*, of specific gravity 1·05 to 1·15, is resolved into oxatolylic acid (iv. 287), carbonic anhydride, and methylic alcohol:

$$\underset{\text{Vulpic acid.}}{C^{19}H^{14}O^5} + 3H^2O = \underset{\substack{\text{Oxatolylic}\\ \text{acid.}}}{C^{16}H^{16}O^3} + 2CO^2 + \underset{\substack{\text{Methylic}\\ \text{alcohol.}}}{CH^4O.}$$

But when boiled with baryta-water, it undergoes a different decomposition, yielding alphatoluic acid (p. 863), oxalic acid, and methylic alcohol:

$$\underset{\substack{\text{Vulpic}\\ \text{acid.}}}{C^{19}H^{14}O^5} + 4H^2O = \underset{\substack{\text{Alphatoluic}\\ \text{acid.}}}{2C^8H^8O^2} + \underset{\substack{\text{Oxalic}\\ \text{acid.}}}{C^2H^2O^4} + \underset{\substack{\text{Methylic}\\ \text{alcohol.}}}{CH^4O.}$$

Vulpates.—Vulpic acid is monobasic. The vulpates of the alkali-metals and alkaline earth-metals are soluble in water, and are easily obtained by treating the acid with water and alkaline hydrates or carbonates. The other vulpates are insoluble, and are obtained by precipitation.

Vulpate of ammonium, $C^{19}H^{13}(NH^4)O^5.H^2O$, forms yellow crystals, which dissolve in water and in alcohol, give off ammonia and water when heated, and are then no longer perfectly soluble in water.—The *barium-salt*, $C^{38}H^{26}Ba''O^{10}.2H^2O$, is obtained by boiling vulpic acid with water and barium-carbonate, and separates from the filtrate on cooling, in light-yellow needle-shaped crystals; but by recrystallisation from alcohol, it is obtained in orange-yellow needles containing a different amount of water.—The *potassium-salt*, $C^{19}H^{13}KO^5.H^2O$, crystallises in light-yellow needles, somewhat sparingly soluble both in water and in alcohol.—The *silver-salt*, $C^{19}H^{13}AgO$, is a yellow easily decomposible precipitate, which dissolves in ammonia, and likewise in boiling water, though in the latter case with partial decomposition. It blackens at 100°, but without much loss of weight.

VULPINITE. Anhydrite from Vulpino, near Bergamo.

VULPULIC ACID. } Syn. with VULPIC ACID.
VULPULIN. }

W

WACKE. Syn. with GRAUWACKE (ii. 842).

WAD. A term applied to ores of manganese of variable composition, consisting mostly of mixtures of the sesquioxide and dioxide of manganese. (See MANGANESE, iii. 813.)

WAGITE. A mineral from Nischni-Jagurt in the Ural, containing 26·0 per cent. silica, 66·9 zinc-oxide, 4·7 water, and 1·55 lime, together with traces of copper and iron, closely allied therefore to hemimorphite, but containing somewhat less water. It forms crystalline coatings of blue to green colour; hardness = 5·0, and specific gravity = 2·707. (Radoszkowski, Compt. rend. liii. 107.)

WAGNERITE. Phosphatofluoride of magnesium, found in the valley of Höllengraben in Salzburg. (See PHOSPHATES, iv. 569.)

WAIFA. The Chinese name of a yellow dyestuff, consisting of the undeveloped flower-buds of *Sophora japonica.*

WALCHOWITE. Retinite from the coal-mines of Walchow in Moravia (p. 98).

WALDHEIMITE. A green mineral resembling actinolite, from the serpentine of Waldheim in Saxony, containing, according to Knop (Ann. Ch. Pharm. cx. 360), 55·58 per cent. silica, 10·65 magnesia, 10·84 lime, 12·64 soda, 5·66 ferrous oxide, 0·36 manganous oxide, and 1·72 alumina. Hardness = 5·0. Specific gravity = 2·957.

WALL LICHEN. *Parmelia parietina.* (See LICHENS, iii. 587.)

WALNUT. *Juglans regia.*—The green shells of the fruit of this tree contain, according to Braconnot, a peculiar bitter principle, together with citric acid, malic acid, tannin, &c. According to Buchner, the alterable constituent of the shells and leaves of walnuts is not tannin, but a peculiar acid, juglandic acid, which, in contact with the air, is converted into a neutral brown insoluble substance called juglandin (iii. 444).

The ripe kernels contain 40 to 50 per cent. of a fat-oil, having a yellow or greenish-yellow colour, a mild taste and odour, and a specific gravity of 0·96. It solidifies at −27°, dissolves sparingly in alcohol, and dries easily in contact with the air. According to Saussure and Hermann, it contains from 79 to 80 per cent. carbon, and 10·5 to 11·0 hydrogen.

According to Vogel and Reischauer (Buchn. Repert. v. 106; vi. 1), fresh walnut-shells contain a peculiar principle, which they call mucin (iv. 143).

The ash of the wood, bark, and leaves of the walnut-tree in spring and autumn has been analysed by Staffel (Ann. Ch. Pharm. lxxvi. 379); that of the nuts themselves by Glasson (*ibid.* lxi. 343):

Ash of the Walnut-tree.

	Wood.		Bark.		Leaves.		Nuts.
	Spring.	Autumn.	Spring.	Autumn.	Spring.	Autumn.	
Ash per cent. of fresh substance . .	0·90	1·47	1·38	3·68	1.09	2·57	0·67
Ash per cent. of dry substance . .	10·03	2·98	8·75	6·40	7·72	7·0	
Potash . . .	40·8	14·9	44·5	11·0	42·0	25·5	27·1
Lime	22·5	55·9	18·4	70·1	26·9	53·6	21·6
Magnesia . . .	8·9	8·1	7·2	10·5	4·8	9·8	7·7
Alumina . . .	. .	. .	. .	0·3	0·2	0·06	
Ferric oxide . .	2·7	2·2	0·8	0·4	0·4	0·5	0·7
Sulphuric anhydride .	4·9	3·1	4·4	0·1	2·6	2·6	2·3
Silicic „ .	2·4	2·8	2·7	0·7	1·2	2·0	1·1
Phosphoric „ .	14·9	12·2	19·9	5·8	21·1	4·0	35·6
Chloride of potassium	3·1	0·6	1·9	0·9	1·0	1·7	0·8

Several preparations from the leaves and young shells of the walnut are used in medicine; the oil of the nuts is used chiefly as a condiment. (Handw. d. Chem. ix. 555.)

WARWICKITE. A mineral occurring at Warwick in New York, in dark-brown or iron-black, indistinct, monoclinic crystals, of specific gravity 3·0 to 3·3. According to Shepard (Sill. Am. J. xxxiv. 313; xxxvi. 85), it contains 27·33 per cent. fluorine, 61·71 titanium, 7·14 iron, 0·80 yttrium, and traces of aluminium. According to L. Smith (*ibid.* xvi. 293) it contains 20 per cent. boric acid.

WASHINGTONITE. Titaniferous iron, from Litchfield, Connecticut (p. 847).

WASITE. This name was given by Bahr (Pogg. An. cxix. 572; Jahresb. 1863, p. 199) to a mineral resembling orthite, from Rensholm, an island near Stockholm, which he supposed to contain the oxide of a new metal, wasium; subsequent experiments, however, have led him to regard this supposed new oxide as most probably identical with thorina (Ann. Ch. Pharm. cxxxii. 227; Jahresb. 1866, p. 207). The so-called wasite contains alumina, ferric oxide, yttria, thorina, the oxides of cerium, lanthanum, didymium, and manganese, lime, and alkali.

WASIUM. See the last article.

WATER. Synonyms, *Wasser. Eau. Aqua. ὕδωρ.* Symbol, H^2O. Molecular weight, 18.—This substance, which plays so important a part in most terrestrial phenomena, was long regarded as an element or simple substance. Towards the end of the last century, however, the observations of Cavendish on inflammable air furnished the material by which Lavoisier was enabled to show that water is a compound of two distinct elementary substances, and thus to supply an important feature of the chemical system he had introduced. (See GAS, i. 780 *et seq.*)

Water occurs universally on the earth in one or other of the physical states which it is capable of assuming. As a liquid it constitutes the great mass of the oceans, seas, rivers, lakes, &c., which cover upwards of three-fourths of the earth's surface. Water also issues from the interior of the earth at many places as springs (pp. 1014, 1015). In the solid state, as ice and snow, it occurs permanently in the polar regions, and in lofty mountain districts, and periodically in the temperate zones. In the state of vapour it occurs invariably as a constituent of the aërial envelope of the earth, and to an extent determined by the temperature and other local conditions. (ATMOSPHERE, i. 437, and CLOUDS, i. 1027 *et seq.*) Water-vapour also occurs abundantly in the exhalations of volcanoes, during eruptions, and is continuously evolved from the interior of the earth at many places, as in Iceland and at the solfatara and fumaroles in the neighbourhood of volcanoes.

Water also occurs mechanically disseminated throughout the mass of the strata underlying the earth's surface, sometimes in considerable proportion, and even the most compact rocks contain a sensible amount of water. In many solid minerals and organic substances it also exists in a state of combination, sometimes to the extent of 40 or 50 per cent. and upwards. Thus allophane contains about 40 per cent. of water, chabasite contains 20 per cent., and brown iron ore 15 per cent. of water. Living plants and animals contain from 80 to 90 per cent. of water.

Properties.—Pure water is perfectly free from taste and smell, and within a range of temperature between 0° and 100° C., under the ordinary atmospheric pressure, it is a transparent, almost colourless liquid. The slight blue colour of water may be observed, as pointed out by Bunsen (Ann. Ch. Pharm. lxxii. 44), by looking at a shining white object through a column of pure water 2 metres long, contained in a tube blackened inside.

The density of water in the liquid state is about 770 times as much as that of atmospheric air, and is greatest at a temperature of about 4° C. (= 39·2° F.) (HEAT, iii. 58 *et seq.*) Taking the density at this temperature as unity, it is 0·999877 at 0° C., and 0·999107 at 15·5° C. The density of water is always taken as the standard of comparison in reference to which the densities of other solid and liquid substances are expressed (see SPECIFIC GRAVITY, p. 357 *et seq.*). In the United Kingdom the density of water at the temperature of 60° F. (= 15·5° C.) is taken as unity; but on the continent the density of water at the temperature of 4° C. is more generally adopted as unity. A cubic centimetre of pure water at this temperature, and under a pressure equal to a barometric column of 760 millimetres of mercury—29·922 inches—weighs 15·432349 grains or 1 gramme, which is the unit of weight in the metric system.

The following table (p. 1010) gives the weights of certain volumes of water in terms both of the metric system and of the system of weights and measures used in the United Kingdom.

Water is slightly elastic. By an increased pressure of one atmosphere its volume is reduced to the extent of ·000045 (Oersted), or ·000047 (Regnault), and under a pressure of 200 atmospheres its volume is said to be reduced $\frac{1}{12}$ (Perkins, Gilb. Ann. lxxii. 173; Pogg. Ann. ix. 554). The compressibility increases as the temperature

Grains.	Cubic centimetres at 4° C. grammes.	Cubic Inches at 62° F.	Pound.	Gallon at 62° F.	Cubic feet at 62° F.
1					
15·432349	1	·061027		·0002201	·0000353
252·456	16·3861759	1			
7000·	454·3457969	27·727	1	·1	·016046
70000·	4543·457969	277·276	10·	1	·16046
436,495	28315·	1728·	62·355	6·2355	1

rises. Thus at 0° C. it amounts to ·0000503; at 10·8° to ·000048; at 35° to ·0000456, and at 53° to ·000041. (Grassi, Ann. Ch. Phys. [3], xxxi. 437. See Elasticity, ii. 370.)

Taking the volume of water at 0° C. as unity, it expands to 1·042986 when heated to 100° C. (Kopp), and to 1·1016 when heated to 156·8°. (Mendelejeff.—See Heat, iii. 58.)

Water has a high capacity for heat, and its specific heat is taken as the standard of unity in reference to which the capacities of other substances for heat are expressed. (Heat, iii. 34.)

Water is a very bad conductor of heat; but when heat is applied to water from below the portion which is heated expands, and thus becoming specifically lighter, rises to the surface, while the colder and denser portion sinks, and is in its turn heated, until the whole mass acquires a uniform temperature. (Conduction of Heat, p. 73.)

At the temperature of 0° C. water becomes solid or freezes, and at the same time expands considerably. In that state it presents as ice crystalline structure, and as snow crystalline forms belonging to the hexagonal system, which are derivatives of the rhombohedron and six-sided prism.

Ice is colourless or slightly bluish, and transparent when it has been formed from water perfectly at rest. Its density is less than that of water at 0° C., or about 0·920 (Dufour, Compt. rend. lvi. 1079.—Duvernoy, Pogg. Ann. cxvii. 454). Consequently ice always floats on the surface of water, and since water attains its maximum density at the temperature of 4° above the freezing-point, it follows that when the water of lakes, rivers, &c., is cooled below that point, the colder portion remains at the surface, and when it reaches the freezing point, is there converted into ice, while the water below remains at 4° C.

The expansion which takes place in the freezing of water, to the extent of nearly $\frac{1}{11}$ the volume of the water, frequently causes the bursting of pipes and other vessels, and it is a powerful agent in the disintegration of rocks. (See Heat, iii. 78 *et seq.*)

Water contained in closed vessels and in a state of perfect rest may be cooled to —10° or —13° C. without becoming solid, and then on the slightest agitation it suddenly solidifies. (Heat, iii. 75.)

The conversion of water at 0° C. into ice is accompanied by liberation of heat, and in the melting of ice heat is absorbed or rendered latent to the same extent, without raising the temperature of the water above 0°, so that by applying heat to a mixture of ice and water, the temperature is not raised above 0° until after all the ice has been melted. The quantity of heat absorbed or liberated in the melting of ice or freezing of water is sufficient to raise the temperature of an equal weight of water to the extent of 79·2° C., so that when 1 pound of ice is mixed with 1 pound of water at 79·2°, the ice is melted and the whole of the water has a temperature of 0° C. (Heat, iii. 77.)

The melting point of ice is reduced slightly below 0° C. by increase of pressure to the extent of 0·00747° C. for each additional atmosphere. (Mousson, Ann. Ch. Phys. [3], lvi. 252. See Heat, iii. 76.)

Water evaporates at all temperatures when in contact with atmospheric air or other gases, and the vapour thus formed has a density and tension determined by the temperature (see Heat, iii. 81, 93). This evaporation takes place only from the surface, and to an extent proportionate to the volume, temperature, and dryness of the air with which the water is in contact. In a confined space this evaporation ceases when the air becomes saturated with water-vapour. In the open air it proceeds more rapidly in proportion to the extent of surface exposed, and when the air, which has become saturated with vapour, is constantly replaced by fresh air. Consequently a rapid current of air favors evaporation.

Under the ordinary atmospheric pressure—760 mm. or 29·922 inches—water boils at the temperature of 100° C., and is converted into upwards of 1600 times its volume of vapour. When the pressure is reduced to near a vacuum, the boiling point is lowered to nearly 0° C.; and it rises when the pressure is increased, as shown in the following table of the results obtained by Arago and Dulong (Ann. Ch. Phys. [2], xliii. 74):-

Pressure in atmospheres.	Temperature.	Pressure in atmospheres.	Temperature.	Pressure in atmospheres.	Temperature.	Pressure in atmospheres.	Temperature.
1	100°	5	153·1	12	190·0	25	226·3
1·5	112·2	6	160·2	14	197·2	30	236·2
2	121·4	7	166·5	16	203·6	35	244·8
3	135·1	8	172·1	18	209·4	40	252·5
4	145·4	10	181·6	20	214·7	45	265·9

The boiling point of water under the ordinary pressure is slightly influenced by the nature of the vessel in which it is heated, and by the state of its surface. Thus in vessels of glass or porcelain, with very smooth surfaces, water boils 1 or 2 degrees higher than in metallic vessels with a rough surface. (See Heat, iii. 87.)

The conversion of water into vapour is always attended with absorption of heat. The quantity of heat absorbed or rendered latent by water at 100° C., in becoming vapour at the same temperature, would raise the temperature of water 5·37 times as much from 0° to 100° C., so that when one pound of water vapour at 100° C. is mixed with 5·37 pounds of water at 0° C., the vapour is condensed and the 6·37 pounds of water have a temperature of 100° C. (See Heat, iii. 96 *et seq.*)

Water-vapour is colourless and transparent, and becomes visible only when partially condensed, as in the case of steam escaping into the atmosphere. The specific gravity of water-vapour at 100° C. is 0·622, as compared with air at the same temperature, and as compared with air at 0° C. it is 0·455.

Water is a very efficient solvent, so much so that there are very few substances, solid, liquid, or gaseous, which are not to some extent capable of being dissolved by water. Many substances, however, can be dissolved by water only in such minute proportions that for most purposes they may be regarded as practically insoluble. Thus calcic carbonate is generally classed among insoluble substance; but since it dissolves in from 10,601? (Fresenius) to 30,000 parts of water, it must be considered as a soluble substance, so far as relates to the character and contents of natural waters, since the above proportion amounts to at least 2·5 grains per gallon, and especially since calcic carbonate in some form or other is so frequently a constituent of the strata with which water comes in contact.

The solubility of different substances in water is very unequal. Some are readily soluble, and require only small proportions of water, others are but sparingly soluble. Generally the solubility of any particular solid or liquid substance is increased in proportion as the temperature is raised. (See Heat, iii. 79; and Solution, v. p. 349.) But there are many exceptions to this rule: thus cold water dissolves calcic sulphate in larger proportion than water at 100° C., and water at 120° C. does not dissolve any. Water at 0° C. dissolves nearly twice as much lime as water at 100° C.

In the case of gases, the amount capable of being dissolved by water is very much dependent on the pressure. Under the ordinary pressure it is generally larger in proportion as the temperature is lower. Thus water at 0° C. dissolves 68·61 times its volume of sulphurous acid gas, while water at 24° C. dissolves only 31·8 times its volume. There are, however, exceptions to this rule; between the temperatures of 0° and 25° C., water dissolves a constant amount of hydrogen, or 0·0193 of its volume. (Gases, Absorption of, i. 791 *et seq.*)

When the solution of a solid substance in water is not accompanied by chemical combination, there is very often a reduction of temperature produced, sometimes to a considerable extent. (See Heat, iii. 79, 80, and 112.) The solution of gases, on the contrary, is generally attended with increase of temperature, partly in consequence of the change of state in the gas.

Aqueous solutions of solid substances have a higher density than water; and, for any given substance, the density is proportionately higher according to the amount of substance in solution. The water-solutions of certain liquids and gases are also denser than water; but in many instances the density of such solutions is less than that of water. For some purposes the degree of density of water-solutions of any particular substance affords a sufficiently accurate indication of the amount of such substance in the solution, as in the case of sugar, soda, sulphuric acid, hydrochloric acid, ammonia, alcohol, &c.

The freezing-point of water-solutions is lower than that of water: thus sea-water freezes less readily than fresh water. When dilute solutions freeze, pure ice is formed, and thus the solution is concentrated. In cold countries salt is often obtained in this way. A solution containing 10 per cent. of common salt freezes at − 6° C.; one with 10 per cent. ammonium-chloride freezes at − 6·5° C.; one with 43 per cent. crystallised calcic chloride freezes at − 10° C., and a saturated solution of calcic chloride freezes at − 21° C. (**Rudorf**, Poggend. Annal. cxiv. 63.)

The boiling-point of water is raised when it contains solid substances in solution, and to an extent proportionate to the amount of substance in solution. (See HEAT, iii. 89.) Liquid and gaseous substances dissolved in water sometimes cause a rise and sometimes a depression of the boiling-point.

Certain liquids when mixed with water form two solutions which do not mix, each liquid acting as a solvent to the other; thus water dissolves 10 per cent. by measure of ether, while ether dissolves about $\frac{1}{36}$ of its bulk of water, and when water is mixed with more ether than it can dissolve, these saturated solutions are formed in two separate layers.

The saturated solutions of solid substances which are capable of crystallising deposit these substances in a crystalline form when the water is evaporated, and the crystals thus produced are generally larger and more regular when the evaporation goes on slowly, and without disturbance of the liquid. (CRYSTALLISATION, ii. 114 *et seq.*)

Water, in its chemical characters, is a remarkably neutral substance, the relatively basylous and chlorous characters of its constituents being so nearly compensated that it is capable of assuming either relation according to the nature of the substance with which it reacts or combines. Its basyl constituent may be replaced, either by a basylous or chlorous substance (METALS and METALLOIDS, iii. 937), so as to produce a great variety of compounds whose constitution is referrible to the type of water.

Water, though itself an eminently neutral substance, often exercises an important influence in determining the chemical activity of other substances, not only as a solvent by rendering one or more of the substances concerned in a particular reaction, liquid, and in so far more susceptible of chemical action, but also by taking part in the reaction itself; thus, for instance, concentrated sulphuric acid and iron present no reaction even when heated to the boiling-point, and this is also the case with concentrated nitric acid, and the metals tin, lead, and iron. When water is added, however, vigorous chemical action is at once set up, and in numerous other instances the presence of water, in some condition, is essential to chemical action. The chemical processes taking place in the organisms of plants and animals require the presence of water, and in the alteration of minerals it is equally necessary, both as the solvent of products of decomposition, and as the medium for rendering efficient the carbonic acid, oxygen, &c., by which alteration is produced.

Composition.—The composition and constitution of water have already been treated of. (HYDROGEN, OXIDES OF, iii. 195.)

Decomposition.—Water may be decomposed in various ways; viz.

1. With liberation of both constituents.

By Heat.—Grove first observed that water is decomposed by heat. Deville considers that this decomposition (*dissociation*) takes place between 1000° and 2000° C., and that at a lower temperature the greater portion of the gases again combine together.

By Electricity.—When two platinum-plates are immersed in a vessel of water, slightly acidulated with sulphuric acid to increase its conducting power, and these plates are connected with the poles of a voltaic battery, hydrogen and oxygen gases are evolved at the surfaces of the plates. If these gases are collected in two glass tubes filled with water and inverted over the platinum-plates, the volume of the hydrogen gas evolved at the one plate will be found to be exactly double that of the oxygen gas evolved at the other plate, except in so far as the greater solubility of oxygen gas in water affects this relation. (ELECTROLYSIS, ii. 432 *et seq.*)

2. With liberation of one constituent only:—

The *metals of the alkalis and alkaline earths* decompose water at the ordinary temperature, disengaging hydrogen and forming oxides. Many other metals decompose water or water-vapour in the same way at temperatures varying from 100° C. to a white heat. Others do not decompose water under the influence of heat alone.—*Iron* and many other metals decompose water at the ordinary temperature, only in the presence of an acid.—*Zinc* and some other metals decompose water under the influence of heat, and in the presence of an alkali.

Carbon also decomposes water-vapour at a red heat, yielding hydrogen, some carbonic oxide, and a little carburetted hydrogen.

Some of the lower oxides decompose water, or water-vapour, with evolution of hydrogen, either at the ordinary temperature or with the aid of heat.—*Hydrated silicious oxide* decomposes water in presence of acids or ammonia, forming silicic acid.—

Carbonic oxide decomposes water-vapour at a red heat, yielding hydrogen and carbonic acid.

Chlorine decomposes water under the influence of light, and water-vapour at a red heat, with formation of hydrochloric acid and liberation of oxygen. Water-vapour heated to redness with *bromine-vapour* in excess, is decomposed in a similar manner. This decomposition is not effected by *iodine.*

3. Both constituents enter into other combinations:—

Phosphorus heated with water in presence of an alkali decomposes it, with formation of phosphoretted hydrogen and hypophosphorous acid. According to Schönbein, water is decomposed when boiled in contact with nitrogen-gas, nitrous acid and ammonia being formed:

$$2H^2O + 2N = (NH^4)NO^2.$$

Many chlorides and bromides decompose water, forming oxides and hydrochloric or hydrobromic acid. Thus *phosphorus chlorides* yield, with water, phosphorous or phosphoric acid and hydrochloric acid:

$$PCl^3 + 3H^2O = 3HCl + PH^3O^3;\ \text{and}\ PCl^5 + 4H^2O = PH^3O^4 + 5HCl.$$

Some metallic chlorides are decomposed by contact with water, forming oxychlorides and hydrochloric acid. (ANTIMONY, i. 318, 327, and BISMUTH, i. 591.)—*Aluminic* and *magnesic chlorides* decompose water when their solutions are boiled, yielding alumina or magnesia, while hydrochloric acid escapes.

Many metallic chlorides, bromides, and iodides decompose water-vapour with the aid of heat, yielding the corresponding oxides and hydrochloric acid. Certain metallic sulphides decompose water-vapour in a similar manner.

Arsenious acid and *sulphurous acid* decompose water in presence of chlorine, with formation of arsenic acid or sulphuric acid and hydrochloric acid.

Certain *oxides* decompose water, with formation of a product containing the elements of both substances. Thus *sulphuric anhydride* and water yield hydric sulphate; *calcic oxide* and water yield calcic hydrate:

$$SO^3 + H^2O = SH^2O^4,\ \text{and}\ CaO.H^2O = CaH^2O^2.$$

Production.—Water is formed whenever hydrogen-gas, or a combustible substance containing hydrogen, is burnt in oxygen or atmospheric air. (HYDROGEN, iii. 192; FUEL, ii. 722; and EREMACUSIS, ii. 497.) Water is also produced when hydrogen, or organic and other substances containing hydrogen, are exposed to a bright red heat in contact with easily reducible metallic oxides or other substances capable of yielding oxygen under those conditions. (OXYGEN, iv. 308.)

Combinations.—Water enters into combination with other substances in various ways. In some of the compounds which it forms, water exists as such, while others more probably contain only its elements in the same relative proportion as in water. (HYDRATES, iii. 179; ATOMIC WEIGHTS, i. 458 *et seq.*)

With many saline and other substances, water combines in definite equivalent proportions, producing compounds which are sometimes capable of assuming regular crystalline forms. In such cases it exists as *water of crystallisation*, and the crystalline form of such substances is essentially connected with the amount of water they contain. The amount of water which may be contained in crystallised substances varies from 1 to 24 atoms, and the same substance may combine with water in several different proportions. Thus borax, crystallised from solution at the ordinary temperature, is combined with 4½ at. of water, and when crystallised between 60° and 80° C., it is combined with 2 at.: in the one case it forms oblique rhombic prisms ($2NaHB^2O^4 + 9aq.$); in the other case, octahedrons ($NaHB^2O^4 24aq.$). Sodic carbonate crystallised from solution at the ordinary temperature forms rhomboidal prisms ($Na^2CO^3 + 10aq.$), at a higher temperature it crystallises as $Na^2CO^3 + 8aq.$, or as $Na^2CO^3 + 5aq.$, and from a boiling solution it crystallises as $Na^2CO^3 + 1aq.$ in rectangular tables.

The presence of water of crystallisation combined with a salt, often influences its colour; thus anhydrous cupric sulphate is white, while the crystalline salt $Cu''SO^4 + 5aq.$ is blue. Anhydrous nickel sulphate is yellow and the crystalline salts are green.

In some cases, water of crystallisation is so feebly combined that it is gradually separated when the substance containing it is exposed to dry air. (EFFLORESCENCE, ii. 362.) Water of crystallisation is always expelled by heat, and generally at a temperature of from 100° to 120° C. Some crystallised substances require a higher temperature; but in any case the crystals become opaque and friable in proportion as the water of crystallisation is expelled, and at last disintegrate and fall to powder. Certain substances retain a portion of their water of crystallisation more tenaciously than the rest. Thus cupric sulphate retains one molecule of water when dried at 100°, and does not give it up until heated to 200° C. (HYDRATES, iii. 180.) Potash-alum loses 10 at. water at 120°, and the remaining 2 atoms are not separated under 200° C. Water of crystallisation may also be abstracted from crystals by immersing them in a liquid which attracts water but does not dissolve the substance. Thus alcohol abstracts water from crystallised sodic sulphate, and oil of vitriol abstracts it from cupric sulphate.

Substances containing water of crystallisation frequently melt with ease when heated, and then become solid again after the heat is maintained some time, and the water of crystallisation has been evaporated.

Many amorphous substances also contain water in a state of combination similar to that in which it exists in crystals.

Substances which are very soluble in water often attract water from the atmosphere to such an extent as to form a solution, and are then called *deliquescent*, as for instance calcic chloride. (Deliquescence, ii. 309.) Many insoluble pulverulent substances also attract water from the air in the same manner, as for instance cupric oxide, silica, &c., and are termed *hygroscopic*. Organised substances, such as wood, hair, &c., have the same property (Hygrometry, iii. 233). Some liquids have the same property, as for instance sulphuric acid.

Natural Water.—The constant evaporation from the surface of all masses of water exposed to the atmosphere, the diffusion of the water-vapour throughout the atmosphere, and its subsequent condensation there to the liquid or solid state, give rise to an incessant circulation of water, which enables it to play an important part in a variety of natural phenomena. Of the total amount of condensed atmospheric vapour falling upon the surface of continents and islands, a certain portion, which varies in different localities according to the relative permeability and configuration of the superficial strata, is absorbed and penetrates downwards, until it reaches a less permeable stratum, above which it accumulates, and taking an underground course, determined by the inclination of the strata, towards some point where they crop out again at a lower level, reappears at the surface as springs along the line of outcrop. It is there discharged into, or forms the source of a stream, and thence flowing along the surface, such streams unite to form a river, which finally falls into the sea. If the permeable or "water-bearing" strata do not crop out again at the surface, but dip down under others which are impervious, the water they absorb may penetrate to very considerable depths, and will not then reappear at the surface as a spring, unless it meets with a fissure through which it may be forced upwards—either by the hydrostatic pressure of the water in the upper extremity of the water-bearing strata, or by some other force acting from below—or unless the overlying strata are bored through so as to form an artificial spring. (See Artesian Wells, *Ure's Dictionary of Arts, Manufactures, and Mines*, i. 192 *et seq.*)

As a consequence of the remarkable solvent power of water, it takes up whatever soluble substances it may meet with in each stage of its passage from the state of vapour in the atmosphere to its discharge into the sea. (Geology, Chemistry of, ii. 834 *et seq.*) For this reason natural water never occurs absolutely pure, and having regard to this circumstance, the different kinds of natural water may be classified under the heads of *rain-water*, *spring-water*, *river-water*, and *sea-water*.

Rain-water approaches nearer to absolute purity than any other kind of natural water. When collected in suitable vessels, it contains only such dissolved substances as it can derive from the atmosphere. These consist chiefly of atmospheric gases—oxygen, nitrogen, and carbonic anhydride, together with organic substance, and particles of dust and such other mechanical admixtures as are sometimes present in the air about towns, factories, &c. (Atmosphere, i. 439 *et seq.*)

The total amount of gases dissolved in rain water is about 25 cubic centimetres per litre. The ratio of the oxygen to nitrogen by volume is greater in this gas than in atmospheric air, on account of the greater solubility of oxygen in water. (Atmosphere, i. 437.—Gases, Absorption of, ii. 790.) Analysis has given the following percentage results by measure:

	Baumert.	Peligot.
Oxygen	33·7	31·2
Nitrogen	64·5	66·4
Carbonic anhydride . .	1·8	2·4

Rain-water probably always contains *ammonia* to some extent, either as carbonate or combined with other acids. The amount is greater just after the commencement of rain than when it has continued for a long time. Boussingault found ·004 grm. per litre in rain-water collected in Paris, and in that collected in the country only ·00079 grm. per litre. Dew he found to contain from ·001 to ·006 grm. per litre. In water condensed from fog he found ·0497 grm., and on another occasion in Paris ·1378 grm. per litre. Barral found from ·002 to ·003 grm. per litre in rain-water collected in Paris

(Ann. Ch. Phys. [3], xxxix. 257; xl. 129). In rain-water collected at Lyons, Bineau found as much as ·03 grm. per litre. The amount of ammonia in rain is also much larger in summer than in winter.

Nitric acid is commonly present in rain-water, chiefly in combination with ammonia. The amount varies considerably, and is greater in rain falling during thunder-storms. Boussingault estimated the average amount at ·0002 grm. per litre. In rain-water, collected during a hail-storm in Paris, he found ·055 grm. per litre, and in the melted hail ·083 grm. per litre; on other occasions from ·0004 to ·0021 grm. per litre in rain-water, from ·0003 to ·004 grm. per litre in snow-water collected in Paris, and in water condensed from fog ·0101 grm. per litre. In the country (Alsace) he found in rain-water from ·00004 to ·00028 grm. per litre; in that collected during a thunder-storm ·0021 grm. per litre; and in water condensed from fog, from ·0004 to ·0018 grm. per litre.—Barral found from ·002 to ·036 grm. per litre in rain-water collected in Paris. The amount is less after rain has continued for some time, and it is generally greater in summer than in winter. (Compt. rend. xxxiv. 283, 824; xxxv. 427; xlvi. 1123, 1175.)

Nitrous acid is also present in rain-water, and according to Schönbein, ammonia-nitrite is formed by the direct combination of nitrogen with water. Lawes, Gilbert, and Way estimate the average amount of nitrogen contained in rain-water, as ammonia, nitrous and nitric acid, at about ·985 grm. per litre. (See Report of the Brit. Assoc. for 1854.)

Rain-water perhaps always contains a small amount of *organic substance*, in consequence of which it readily becomes putrid when kept some time. Angus Smith found 0·01 grm., Marchand ·024 grm., and Chatin ·05 grm. per litre.

Sulphuric acid is often found in the rain-water falling in towns, and near factories where sulphurous gas is generated and discharged into the atmosphere. A. Smith found ·1 grm. per litre in rain-water collected at Manchester.

Rain-water sometimes contains a very small amount of *hydrochloric acid, sodic* or *calcic chlorides*, and other *saline substances*. Barral found the rain-water collected in Paris gave, on evaporation to dryness, a residue amounting to ·022 grm. per litre, and that collected in the neighbourhood of Paris ·0078 grm. per litre.—A. Smith also found a minute quantity of coal-ash in rain-water collected in Manchester.

Rain-water is stated by some observers to contain *iodine*. (Chatin, Compt. rend. xlvi. 399; l. 420; li. 496.—Marchand, *ibid.* xlvi. 806.—De Luca, *ibid.* xlvii. 644; xlix. 170; li. 177.)

Spring-water, whether derived from natural or artificial springs, or from wells, always contains a very much larger amount of dissolved substance than rain-water does, in consequence of its having been for some time in contact with strata from which it has extracted various constituents, partly by its own solvent action, and partly by the aid of the carbonic anhydride originally contained in it as rain-water or derived from subterranean sources. The amount and nature of such dissolved constituents vary of course according to the kind of strata traversed by the water, and the distance that it may have passed through them since the time when it fell as rain upon the surface of the earth.

The depth from which spring-water rises to the surface is in some cases not more than a few feet, in others it rises from very considerable depths. The water of the artesian well at St. Grenelle rises from a depth of 1,800 feet, and the water of many natural springs probably rises from still greater depths.

The temperature at which spring-water issues from the surface differs from a few degrees above 0° C. up to 100° C. With the exception of those springs which occur in mountain ranges near the limits of perpetual snow, and are supplied from glaciers, &c., and some of those which are situated near active volcanoes, there appears to be an intimate connection between the temperature of spring-water and the depth from which it rises. The probable existence of such a relation has received considerable support from the fact that the water from artesian wells has been observed to have a temperature higher in proportion to the depth from which it rises. Thus the water of St. Grenelle has a temperature of 28° C. In many cases the temperature of spring-water presents little or no variation throughout the year. Those kinds which have the highest temperature appear to be most constant in this respect, and to have maintained a uniform degree of heat for many years. Even cold spring-water has a temperature more or less above the mean local temperature of the places where it issues from the earth, and it is only those kinds of spring-water rising from depths within the influence of the local atmospheric changes of temperature, that present any considerable variation of temperature in the course of the year. The mean temperature of such spring-water is either the same as the mean local temperature or but very little above it.

As a rule the general character of the dissolved contents of spring-water does not present much variation except in so far as concerns the relative proportions of the

To face page 1016.

soli… nts… 000,0…	GASEOUS CONTENTS: Cubic cent. per litre. CO².	O.	N.	AUTHORITY.
	trace	. .	. .	Graham, Miller, and Hofmann, *Report on the Chemical Quality of the Metropolitan Water Supply*, Q. J. Chem. Soc. Lond. iv. 376.
·4	,,	. .	. .	
	,,	. .	. .	
	,,	. .	. .	
·1	. .	. .	. .	Campbell, Q. J. Chem. Soc. Lond. ix. 22.
	57·2	. .	. .	Graham, Miller, and Hofmann, Q. J. Chem. Soc. Lond. iv. 376.
	46·6	. .	. .	
·6	49·7	. .	. .	
·5	30·4	. .	. .	Abel and Rowney, Q. J. Chem. Soc. Lond. i. 97.
·7	. .	. .	. .	Campbell, *loc. cit.*
	. .	. .	. .	Brande, Q. J. Chem. Soc. Lond. ii. 345.
·7	. .	. .	. .	Odling, Chem. News, iii. 35.
·4	. .	. .	. .	Graham, Mem. Chem. Soc. Lond. ii. 392.
	16·4	. .	. .	Mitchell, Q. J. Chem. Soc. Lond. ii. 32.
	49·7	. .	. .	Graham, Miller, and Hofmann, *loc. cit.*
·4	0·7	3·4	20·5	Odling, Chem. News, iii. 35-49.
·7	93·6	. .	. .	Clark and Medlock, Q. J. Chem. Soc. Lond. vi. 115.
	34	. .	. .	Mitchell, Q. J. Chem. Soc. Lond. iii. 1.
	82·3	. .	. .	Clark and Medlock, Q. J. Chem. Soc. Lond. vi. 115.
	95·1	. .	. .	
	. .	. .	. .	Noad, Q. J. Chem. Soc. Lond. iv. 20.
	. .	. .	. .	
	. .	. .	. .	
	. .	. .	. .	
	83·5	. .	. .	Robson, Q. J. Chem. Soc. Lond. iv. 7.
	81·8	. .	. .	Barrat, Q. J. Chem. Soc. Lond. xii. 52.
	86	. .	. .	Kynaston, Q. J. Chem. Soc. Lond. xii. 57.
	. .	. .	. .	Giles, Pharmaceutical Journal, viii. 75.
·5	. .	. .	. .	R. A. Smith, *Communicated.*
	. .	. .	. .	Muspratt, Chem. News, ii. 242.
	. .	. .	. .	Phillip.
·8	5·2	. .	. .	Muspratt.
·7	25	. .	. .	
	9·9	. .	. .	Abel, Phil. Mag. (4), xix. 330.
·2	. .	. .	. .	Huggon, Brit. Assoc. Rep. for 1858, p. 51.
	1·5	3·6	13	Payen, Ann. Chim. Phys. (3), i. 381.
	65	2·4	4	Henry.
	. .	. .	. .	Letzko and Weiner.
	. .	. .	. .	
	. .	. .	. .	Vlaanderen.
	. .	. .	. .	Gunning.
	. .	. .	. .	
	. .	. .	. .	
	. .	. .	. .	Johnstrug, Arch. for Ph. og techn. Chme.

SOURCE.	Height above Sea Level.	Name of Spring.	ITS: PARTS IN 1,0 Te ra- °.	Fl.	
Vichy, France	. .	Puits Carré . .	4 5·8	. .	
Chaudesaigues, France	. .	Par . . .	8 2	. .	
Bilin, Bohemia	. .	Josephsquelle .	9·7	. .	
Ems, Nassau	. .	Kesselbrunnen .	4 8·7	·1	
Fachingen, Nassau . . .	. .	. . . . .	4·7	. .	.
Teplitz, Bohemia	. .	Steinbad . .	4 8·5	. .	
Spa, Belgium.	1000	Pouhon . .	9	. .	
Weilbach, Nassau (1835) . .	1100	. . . . .	1 5·2	. .	
Karlsbrunnen, Silesia	2353	. . . . .	9·6	. .	
Pfäffers, Switzerland . . .	2116	. . . . .	4 4·1	. .	
Töplitz, Illyria	. .	. . . . .	3 2·4	. .	
Carlsbad, Bohemia . . .	1170	Sprudel . .	7 9·1	1·5	
Püllna, „	. .	. . . . .	4	. .	
Saidschütz, „	. .	Chief Spring .	3·4	. .	
Seidlitz, „	. .	. . . . .	8·6	. .	
Pyrmont, Waldeck	. .	. . . . .	1 8·1	. .	
Bath, Somersetshire	. .	King's Bath . .	9·5	. .	
Cheltenham, Gloucestershire . .	. .	Royal Well . .	1 9·1	. .	2
Wiesbaden, Nassau	. .	Kesselbrunnen .	6 3·7	. .	
Selters, „	800	. . . . .	1 28·4	1·5	
Aix-la-Chapelle, Rhenish Prussia .	. .	Kaiserquelle . .	76·1	. .	
Harrogate, Yorkshire	. .	Old Sulphur Well .	18·2	. .	
Wheal Clifford, Cornwall . .	–1320	. . . . .	5 23·8	. .	
Atlantic Ocean	41° 18′ N.	36° 28′ W.	29·8	. .	2
„	20° 54′ N.	40° 44′ W.	46·3	. .	1
„	0° 47′ S.	35° 20′ W.	77·5	. .	1
„	23° 45′ S.	29° 27′ W.	91·6	. .	1
„ off Cape Horn . .	56° 32′ S.	68° 47′ W.	77·9	. .	1
Pacific Ocean, 11 feet deep . . .	25° 11′ S.	93° 24′ W.	86·4	. .	1
„ 420 „	„	„	26·6	. .	1
„ Algodon Bay . . .	22° 6′ S.	70° 16′ W.	45·3	. .	2
„ Callao Harbour . .	12° 5′ S.	77° 14′ W.	94·9	. .	1
German Ocean	51° 9′ N.	3° 8′ E.	62·8	. .	1
„			28·3	. .	2
„ between Belgium and England			90·2	. .	
„ some miles off Havre			82·5	. .	
„ off Heligoland			80·2	. .	
Baltic			18·9	. .	
Mediterranean, from the Lagunes of Venice			62·1	. .	
„ from Leghorn Harbour			01·7	. .	
„ off Cette, about 3,500 metres from shore . .			42·8	. .	2
„ off Marseilles			15·9	. .	2
Black Sea, off southern coast of Crimea			50·2	. .	
Sea of Azof, between Kertch and Mariapol			14·5	. .	
Caspian Sea, 2 werst S.W. of Pischnoi			37·2	. .	
Dead Sea			179	. .	1

The gaseous contents of mineral water also vary considerably in amount. In some cases it is very small, in others so large that the gas is evolved from the water as it ascends, and the water issues together with a copious discharge of undissolved gas. The constituents of the gaseous contents of mineral water are chiefly *carbonic anhydride, nitrogen*, and *oxygen*, sometimes also *sulphuretted hydrogen* and *carburetted hydrogen*.

Since the difference between the various kinds of mineral water consists chiefly in the nature and relative amount of their dissolved contents and in the proportions which the constituents of those contents bear to each other, they may be conveniently classified according to the predominance of some one or other constituent, and on this principle they may be arranged under the following heads, viz:

I. *Carbonated water*, in which the saline contents consist chiefly of carbonates. According to the nature of the basic constituent present in largest proportion, such water may be either:

1. Alkaline, like the water of Vichy, Bilin, Ems, Fachingen, Töplitz, &c.
2. Magnesian, like that of Schwalbach, Göppingen, Spa, &c.
3. Calcareous, like that of Griessbach, Karlsbrunnen, etc.

Mineral water belonging to any one of these subdivisions may also contain ferrous carbonate, and is then termed *chalybeate*, as for instance, the water of Spa.

If the water contains a large amount of carbonic anhydride in solution it is termed *acidulous*, like the water at Vichy, St. Nectaire, Fachingen, &c., and when it contains sulphuretted hydrogen, it is called sulphuretted, like the water at Schinznach.

II. *Sulphatic* water, in which the saline contents consist chiefly of sulphates, and, according to the preponderating basic constituent, this may be either:

1. Alkaline, like the waters of Carlsbad, Bristol, Püllna, Sebastiansweiler.
2. Magnesian, like the water of Saidschütz.
3. Calcareous, like the water of Pyrmont, Epsom, Bath, Schwarzsee.

Sulphatic water sometimes contains ferrous sulphate, and is then termed *chalybeate*. Sometimes it contains a large amount of carbonic anhydride in solution, and is then termed *acidulous*, as in the water of Carlsbad, Pyrmont, and it is frequently *sulphuretted*, like the water of Schwarzsee, Sebastiansweiler.

III. *Chlorinated water*, in which the saline contents consist chiefly of chlorides, and is, according to the preponderating basic constituent, either:

1. Alkaline, like the water of Wiesbaden, Leamington, Harrowgate, Cheltenham, Selters, Homburg, Kissingen, Kreutznach, Alexisbad, Aix-la-Chapelle, Weilbach.
2. Magnesian, like the water of the Dead Sea, Elton lake, and some other lakes of eastern Europe and Asia.

Chlorinated water is sometimes *chalybeate*, and may contain both ferrous sulphate and chloride, or ferrous carbonate, like the water of Alexisbad, Homburg, Hermannsbad. It is sometimes also *acidulous*, like the water of Homburg, Kissingen, and Wiesbaden, and sometimes *sulphuretted*, like the water of Harrowgate, Aix-la-Chapelle, Weilbach.

IV. *Silicious water*, in which the saline contents consist chiefly of silicates, like the hot spring-water of Iceland.

The accompanying table contains the analyses of some of the most celebrated kinds of mineral water, which have been selected as types of the several classes above described.

River-water, though generally originating to a great extent from natural springs, almost always contains a smaller amount of dissolved contents than the generality of fresh spring-water. This is partly the result of dilution by the direct influx of rain or some other form of meteoric water, glacier streams, &c., and is sometimes also in part due to the disengagement of carbonic anhydride when the water of the springs feeding a river comes in contact with atmospheric air as a flowing stream, and there is a consequent separation of substances which, like calcic carbonate, &c., were chiefly held in solution by that gas in the spring-water.

The total amount of dissolved contents in river-water varies less than in spring-water. It rarely exceeds from ·3 to ·4 grm. per litre, and is sometimes very much less in the case of rivers flowing through districts where crystalline or schistose rocks prevail, when the water is sometimes almost as pure as rain-water. The gaseous contents are the same as in fresh spring-water, but the amount of carbonic anhydride is generally less than in most spring-water, and from the free exposure of the water to the atmosphere, the proportion of oxygen to nitrogen, under normal conditions, is the same as in rain-water, or as 1 to 2 by volume, being greater than in atmospheric air in consequence of the greater solubility of oxygen in water. (See ATMOSPHERE, i. 437, and GASES, ABSORPTION OF, ii. 790.)

The amount of dissolved *organic substance* in river-water is generally much greater than in spring-water. This is due to the surface drainage of river-basins being discharged into the rivers, which are the natural drains of the country they flow through. The organic substance thus constantly carried into rivers, and diffused throughout the running water containing dissolved oxygen, is exposed to its influence and gradually decomposed, being ultimately converted into the final products of such change, viz., carbonic anhydride, water, ammonia, nitrites, and nitrates (EREMACAUSIS, ii. 497). Thus the oxygen dissolved in river-water, and constantly renewed by the contact of the flowing water with the atmosphere, plays an important part in the natural purification of rivers, and in preventing the putrefaction or accumulation of organic substance in their water. In the case of rivers flowing through populous districts, and receiving the drainage of the towns situated within their basins, in addition to the natural surface drainage, the quantity of putrescible organic substance thus constantly carried into the rivers as sewage may be so large that this natural process of purification is inadequate to prevent putrefactive change, especially during hot weather, when the temperature of the water rises considerably (FERMENTATION and PUTREFACTION, ii. 623, *et seq.*). The condition of the Thames within London, during the autumn of 1859, when the sewage of the whole population was discharged directly into it, affords an illustration of the consequences of such contamination of a river. Some observations made by Professor Miller at that time on the gaseous contents of the water taken at different points of the Thames at low water, also serve well to elucidate both the natural process of purification taking place in river-water, and the influence of sewage contamination on the condition of the water, as will be seen from the following tabular statement:

Thames water taken at	Kingston.	Hammersmith.	Somerset House.	Greenwich.	Woolwich.	Erith.
	cub. cent.	cub. cent.	cub. cent.	cub. cent.	cub. cent.	cub. cent.
Total amount of gas per litro	52·7	. .	62·9	71·25	63·05	74·3
Carbonic anhydride .	30·3	. .	45·2	55·6	48·3	57·
Oxygen . . .	7·4	4·1	1·5	·25	·25	1·8
Nitrogen . . .	15·0	15·1	16·2	15·4	14·5	15·5
Ratio of oxygen to nitrogen	1 : 2	1 : 3·7	1 : 10·5	1 : 60	1 : 52	1 : 8·1

From these results it will be seen that while the water at Kingston was in a normal state of aëration, the influence of sewage contamination in abstracting oxygen began to become evident at Hammersmith. At Somerset House it was still more marked, and at Greenwich and Woolwich the oxygen had been almost entirely consumed; but by the time the water reached Erith its state of aëration had greatly improved as regards oxygen. (See also R. A. Smith, Mem. Philos. Soc. Glasgow, vi. 154, *et seq.*)

In addition to the dissolved contents of river-water, saline, organic, and gaseous, it almost always contains *mechanically suspended substance*, the amount of which varies according to the quantity of rain passing into the rivers at different seasons, and also according to the nature and extent of the surfaces drained by them. The amount of suspended substance in the Thames is sometimes as much as ·5 grm. per litre at low water, and ·2 grm. per litre at high water. In the Seine at Paris, the amount of suspended substance varies from ·007 to 118 grm. per litre; in the Rhine at Bonn it is from ·017 to ·205 grm. per litre; and in the Meuse from ·014 to ·474 grm. per litre. In the water of the Mississippi the average amount of suspended substance is about ·8 grm. per litre; in that of the Ganges it is stated to vary from ·2 to 2· grm. per litre, and in that of the Yellow River to be still larger.

The water of lakes which are situated among crystalline or schistose rocks, and have an outlet, is sometimes almost as pure as rain-water. Lakes through which rivers flow, as the Rhone flows through the lake of Geneva, may be considered as mere local expansions of the rivers, and their water will have nearly the same dissolved contents as the river-water. On the contrary in lakes which have no outlet, like the Dead Sea, and many of the salt-water or soda lakes of Eastern Europe, Asia, Africa, and America, the water though sometimes fresh, is often so highly charged with saline substances, which have accumulated by the evaporation of the water flowing into the lakes, that in the dry season certain of the saline contents are deposited, as in the case of the salt lakes of Russia, Central Asia, Africa, and America (p. 184); the soda lakes of Egypt, Asia, Mexico, and Hungary; the borax lakes of Thibet, &c.

mpe-ure. air.	Organic.	GASEOUS CONTENTS: Cub. cent. per litre.			AUTHORITY.
		CO².	O.	N.	
13°	49·7	5·1	. .	. .	Clark, Q. J. Chem. Soc. Lond. i. 155.
. .	32·7	63·1	. .	. .	Graham, Miller, and Hofmann, *Report on the Chemical Quality of the Metropolitan Water Supply*, Q. J. Chem. Soc. Lond. iv. 376.
. .	43·9	50·3	. .	. .	
. .	39·3	43·2	. .	. .	
. .	21·4	50·7	. .	. .	
. .	34	46	. .	. .	
. .	37	63·2	. .	. .	
. .	100	27·2	. .	. .	Ashley, Q. J. Chem. Soc. Lond. ii. 74.
. .	58·2	71·6	. .	. .	Bennett, Q. J. Chem. Soc. ii. 195.
. .	37·3	37·8	. .	. .	Graham, Miller, and Hofmann, *loc. cit.*
. .	39·4	54·2	. .	. .	
. .	59	46·3	. .	. .	
. .	. .	1·5	6·4	14·1	Frankland and Odling, *Report to the Royal Commission on Water Supply.*
. .	. .	2·3	6·3	12·9	
. .	. .	2·9	6·4	13	
. .	. .	1·1	6·4	12·9	
. .	. .	2·3	6·7	13·1	
. .	9	7·9	7·5	14	J. S. Way, communicated by G. W. Hemans, Esq. The Estimation of Gases from Frankland and Odling's Report.
. .	9	1·8	7·4	14·2	
. .	5	1·8	7·5	15·5	
. .	11	·8	7·3	14·4	
. .	11·4	·3	9·3	18·4	Wallace, Brit. Ass. Rep., 1862, p. 94.
1·2°	68·6	22·3	11·1	24·9	R. A. Smith, *Communicated.*
0·8°	30	15·1	9·5	24·8	
. .	26·1	. .	. .	. .	Penny, *Communicated.*
. .	. .	. .	. .	. .	Colin.
. .	8·2	5·8	6·8	15·6	Maumene, Compt. rend. xxxi. 270.
. .	10·7	5·9	7·7	17·6	
. .	40	. .	. .	. .	Tingry.
. .	. .	17·8	9·5	18·2	Deville, Ann. Ch. Phys. xxiii. 32.
. .	6	. .	. .	. .	Tingry.
. .	. .	8·4	8	18·4	Deville, *loc. cit.*
. .	. .	. .	. .	. .	
. .	. .	1·8	20·2		Deville.
. .	. .	17	7·9	15·7	
. .	. .	. .	. .	. .	Pagenstecher.
. .	. .	. .	. .	. .	
. .	3·3	. .	. .	. .	Pagenstecher.
. .	. .	7·6	7·4	15·9	Deville, *loc. cit.*
. .	. .	. .	. .	. .	Bischof.
. .	48	. .	. .	. .	Müller, Arch. Pharm. (2) xlix. 10.
. .	. .	. .	. .	. .	Gunning.
. .	. .	. .	. .	. .	Bischof.
. .	. .	. .	. .	. .	Bauer.
. .	. .	. .	. .	. .	Bischof.

Sea-water is essentially a chlorinated alkaline mineral water, the saline contents of which consists chiefly of sodic, magnesic, potassic, and calcic chlorides and sulphates, together with a number of other substances in much smaller proportion and some in very minute amounts.

The total amount of dissolved contents in the water of the ocean at long distances from land varies from about 28 to 39 grms. per litre. It is largest near the equator and smallest near the poles. The greater evaporation of water in tropical regions than in temperate or polar regions, and the unequal influx of fresh water from rivers or as rain, tend to produce local differences, which are to a great extent compensated by currents. Forchhammer fixes the mean amount of dissolved contents in the water of the ocean at 34·404 grms. per litre (Phil. Trans. clv. 203 *et seq.*). In the water of seas which are partly shut in by land, the amount of dissolved contents is influenced by the amount of evaporation relatively to the quantity of fresh water carried into them by rivers. Thus in the water of the Baltic, the amount of dissolved contents varies from about 5 to 18 grms. per litre at different parts, while in the Mediterranean it varies from about 36 to 40 grms. per litre.

In the water of the ocean there appears, according to Forchhammer, to be generally but little variation in the relative proportions of the chief constituents of its contents, as will be seen from the following table, deduced from the mean results of his numerous analyses:

	SO^4.	Mg.	Ca.	Total saline contents.	Chlorine.
Maximum	14·51	6·768	2·257	181·40	100
Mean	14·26	6·642	2·114	181·10	100
Minimum	13·98	6·570	2·050	180·60	100

Some of the analyses of sea-water indicate much greater local variations in the relative proportions of certain substances, and it is very probable that a variety of circumstances, such as submarine springs or volcanic eruptions, &c., may tend to affect the composition of its dissolved contents either permanently or for a time at certain points.

In addition to the substances already mentioned, sea-water contains about ·3 grm. per litre of *bromine*, and very minute amounts of *iodine* and *fluorine*; also *silica, phosphoric acid* (Voelcker, Chem. Gaz. viii. 346), *calcic* and *magnesic carbonates* in small proportions. The amount of carbonates is largest near the land, and is very small in the water of the ocean (J. Davy, Ed. New Phil. Journ. xlvii. 320). *Silver, lead, copper,* and *arsenic* have been detected either in sea-water, the ashes of marine plants or animals, or in the deposit formed inside the boilers of ocean steamers (Malaguti, Durocher, Sarzeaud, Ann. Chim. Phys. [3], xxviii. 122.—Field, Chem. Gaz. 1857, p. 93.—Daubree, Compt. rend. xxxii. 827). In fact since the ocean is the common recipient of by far the greater part of the water discharged from springs and constituting rivers, most of the material abstracted by their water from the interior and surface of the earth passes into it, and all substances which exist in spring-water may be expected to exist, to some extent, in sea-water.

The gaseous contents of sea-water are nitrogen, oxygen, and carbonic anhydride, amounting altogether to from 10 to 30 c.c. per litre, according to different observers. The amount appears to be greater at a depth of about 2,000 feet than near the surface, but at about 4,000 feet the water contains scarcely any dissolved gases. The relative proportions of the gases have not been estimated with much accuracy. Carbonic anhydride is stated to vary from 2 to nearly 40 c.c. per litre; oxygen from about 1 to 3 c.c. per litre, and nitrogen from 12 to 17 c.c. per litre. (Aimé, Pogg. Ann. lx. 404.—Hayes, Sill. Am. J. 1851, 421; Compt. rend. vi. 616.—Lewy, Ann. Ch. Phys. ii. 535, viii. 425, xii. 5.—Bischof, Chem. Phys. Geol. i. 113.—Thorpe, Chem. Soc. J. [2] v. 189.)

From the facts already stated as to the dissolved contents of the various kinds of natural water, it will be possible to form some general idea of the geological importance attaching to the constant circulation of water from the ocean to the land by evaporation, and then back again to the ocean, after having penetrated through the rocks constituting the land, to various depths in the interior of the earth.

The mere mechanical action of the water discharged by rivers, in abrading the rocks with which it comes in contact after falling as rain, in sweeping away the particles detached by it and by other disintegrating influences, and in transporting the finely divided débris to the ocean, is alone a very potent agent of geological change. The quantity of solid material thus conveyed from the land to the sea, as mud, by such rivers as the Amazon, Yang-tse-Kiang, Mississippi, Nile, Ganges, and Danube, is enormous. It has been estimated that the suspended material annually discharged into the sea by the Mississippi is equal to 4,000 million cubic feet of clay, and that the quantity thus conveyed into the Bay of Bengal by the Ganges and Brahmapootra amount to ten times as much. (Lyell's *Principles of Geology.*)

But the suspended mud of rivers constitutes only a part of the material they convey into the ocean. A further and probably equal quantity is discharged into it in a state of solution. The compositicn of the dissolved material carried into the sea by rivers differs widely from that of the dissolved contents of sea-water, as will be seen from the following comparison of the relative proportions of the chief constituents in both cases:

	CO^2.	Ca.	K.	SO^4.	SiO^2.	Mg.	Na.	Cl.
Dissolved contents of sea water . .		2·114	·305	14·26	trace	6·64	57·	100
" " river-water	807·	568·	43·	228·	10·	36·	43·	100

From this comparison it will be seen that precisely those substances which are present in the dissolved contents of sea-water in the smallest amount, relatively to chlorine, exist in the dissolved contents of river-water in the largest amount relatively to chlorine, and are carried into the sea in the largest quantities. These substances, however, do not accumulate in sea-water; but are abstracted from it by marine plants and animals, whose growth is probably to a great extent supported by the dissolved material conveyed into the sea by rivers, and its chief constituents are found in the ashes of marine plants, and in the shells or skeletons of marine animals. (See CORAL, ii. p. 84; SEAWEED, v. p. 212; SPONGE, v. p. 403.) Consequently the action of water in transporting material from the land to the sea, appears to be one of the conditions essential to the existence of marine organisms, and to the formation of submarine deposits, either through their agency or by simple subsidence. (See GEOLOGY, CHEMISTRY OF, ii. 835.)

The amount of sodic and magnesic chlorides carried into the sea by rivers is small, but as these salts probably accumulate in the water, and as the supply from the land, through the agency of water evaporating from the ocean, is continuous, there is some ground for the opinion that the saline contents of sea-water are very gradually augmenting, and indeed that in their present amount they may be altogether the result of the same process continued during long geological periods. In the water of the Baltic and still more in that of the Mediterranean, it has been ascertained with tolerable certainty, that such an augmentation of the saline contents is going on. The evaporation from the Mediterranean, under the influence of hot dry winds from Africa, is so much greater than the supply of fresh water by rivers, that a current of salt water is constantly flowing in from the Atlantic, through the straits of Gibraltar. The water of the Mediterranean consequently contains a larger average amount of saline contents than that of any other sea communicating with the ocean. Moreover, since the amount is greater at considerable depths than it is near the surface, it appears that by the evaporation of the water at the surface, it becomes denser and sinks towards the bottom. In many places the Mediterranean is upwards of 6,000 feet deep, but at the Straits of Gibraltar the depth is only 1,320 feet, so that although there is an outward deep current into the Atlantic, the denser water below that depth cannot flow out. A similar process of concentration is going on in the Dead Sea, and Caspian Sea, in the salt lakes of Russia, and the soda lakes in Egypt and Hungary, which receive either the water of rivers or of springs, and have no outlet for their water but by evaporation.

The vast quantity of material continually being abstracted from the solid mass of the earth by the water of springs, obviously indicates considerable progressive alteration of the rocks from which it is derived. As regards the contents of fresh water, its chief constituents are probably obtained, for the most part, by direct solution. This may also be the case with some kinds of mineral water; but as regards those kinds of mineral water which contain alkaline and ferrous carbonate, &c., together with large amounts of carbonic anhydride, it is more probable that their dissolved contents originate from the chemical alteration of rocks. This is especially the case when the high temperature of the water indicates that it comes from a great depth, where the degree of heat and other conditions obtaining, may be sufficient to determine reactions which do not take place at the surface of the earth. Without having recourse to any theory respecting the former condition of the earth, and its material elements, it is possible to arrive at a probable inference as to the chemical ehanges involved in the production of the various kinds of mineral-water, simply by a consideration of the state in which the substances they contain exist in rocks, or in those minerals which are the most abundant constituents of known rocks, and of the effects which would result under the influence of such conditions as the characters of mineral water testify to the existence of at the seat of their production.

One of the most striking phenomena presented by mineral water is the frequent and abundant occurrence of carbonic anhydride, either dissolved in the water or discharged together with it, and sometimes in enormous quantity, a single spring often yielding annually upwards of a hundred tons, and some artificial springs, like the artesian wells of Neusalzwerk and Nauheim, yielding respectively from 1,300 to 2,000 tons of this gas in the course of the year. Among the gases associated with mineral water, carbonic anhydride not only occurs in the largest amount; but also exercises considerable influence on the character of the water, in many cases, by determining the solution of calcic, magnesic, and ferrous carbonates, &c. From the frequent occurrence of this gas in connection with volcanic phenomena, and the very general distribution of calcic and magnesic carbonates in rocks, it is probable that the action of subterranean heat upon such rocks gives rise to the production of carbonic anhydride, either by direct decomposition, or more probably by determining the reaction of these carbonates with the silica of silicious rocks, in such a manner as to form products which, like lava and basalt, contain both lime and magnesia combined with silica. Carbonic anhydride may also originate from the decomposition of organic remains in rocks, and from their oxidation by reducible substances such as ferric oxide, and it may be to some extent produced by a subterranean process of combustion, either of carbon, or carbonaceous substances by atmospheric oxygen conveyed into the interior of the earth by water. The occurrence of nitrogen together with the carbonic anhydride evolved from springs, and in volcanic districts, gives some probability to the opinion that the carbonic anhydride may originate partly in this way.

But whatever be the precise mode in which the carbonic anhydride associated with mineral water may originate, its abundant existence in solution at great depths, and consequently under great pressure, is beyond doubt. For that reason, a consideration of the action of such a solution upon rocks of the kind which may be supposed to exist at those depths, is of great interest as regards the production of mineral water. Struve found that a number of silicious rocks were decomposed when exposed to the action of water saturated with carbonic anhydride under considerable pressure, and that the substances dissolved by the water almost exactly corresponded with the dissolved contents of various kinds of mineral water. Thus, for instance, in operating upon phonolite in this way, the substance dissolved contained sodic, calcic, and magnesic carbonates and silica, almost in the same relative proportion as the carbonated alkaline water of Bilin. Basalt and felspathic porphyry yielded substances corresponding to the dissolved contents of the Eger, Marienbad, and Töplitz water. It may, therefore, be inferred with considerable probability that the decomposition of such silicates as constitute those rocks, by water containing a large amount of carbonic anhydride, is the source of the alkaline carbonates in mineral water, and to a great extent also of the calcic, magnesic, and ferrous carbonates it contains. Some idea may be formed as to the magnitude of this process of subterranean alteration, from the fact that the mineral water of Vichy alone brings up annually from the interior of the earth about 1,000 tons of sodic carbonate, while the water of the Carlsbad springs brings up at least ten times as much. The occurrence of kaolin, steatite, serpentine, and a variety of similar mineral substances, may be regarded as a phenomenon correlative to such a decomposition as that by which the alkalis or other bases of felspar, augite, or hornblende, are extracted in the production of mineral-water, and those minerals may represent the residual parts of rocks decomposed in this manner during very remote periods. It would be out of place here to enter more fully into the subject of mineral alteration by water containing various substances in solution, than to point out that the conditions under which mineral water comes into contact with rocks at great depths are peculiarly favourable to the production of many of those changes of minerals and rocks which have hitherto been ascribed to imaginary causes, without a sufficient knowledge of their chemical features. (See GEOLOGY, CHEMISTRY OF, ii. 833; PSEUDOMORPHS, iv. 374; and Bischof, Chem. Phys. Geology.)

The *nitrogen* which is so frequently associated with mineral water, either in its gaseous contents, or in the gases discharged with it from springs, does not appear in all cases to consist merely of that atmospheric nitrogen which may be conveyed, in solution by the water, from the surface to the place where it acquires its saline contents, although that may sometimes be the case, especially when the nitrogen is accompanied by oxygen. The proportion of nitrogen to the other gases, and the actual quantity discharged is sometimes so large—as, for instance, at the Bath springs, where it amounts to about 250 cubic feet daily—that there are probably other sources of this gas, such as the slow decomposition of organic remains. Its occurrence has also been referred to an assumed process of subterranean oxidation of metals by atmospheric air, which is supposed to penetrate in some way to great depths in the interior, and in conjunction with the reaction of water on these metals to give rise not only to the phenomena of thermal springs, but also of earthquakes and volcanoes. (See Daubeny, Description of Volcanoes, Earthquakes, and Thermal Springs.—Bischof, Chem. Phys. Geology.—Lecoq, *Les Eaux Minérales.*

The *sulphuretted hydrogen* present in some kinds of mineral-water originates from the reduction of sulphates by carbonaceous substance and the decomposition of the sulphides by carbonic anhydride.

Quality of Water used for economic and technical purposes.

Since natural water is never absolutely pure, it is evident that as regards the water derived from any particular source, its fitness for ordinary use will depend chiefly upon the amount and nature of the substances which may be present in a state of solution, and perhaps also mechanically suspended in the water. For drinking and for many other purposes, water which is perfectly clear and colourless is sensibly preferable to such as is turbid and coloured, in consequence of its containing suspended impurities whether they consist merely of earthy mud, or of minute living organisms. In this respect, spring or well-water, which undergoes a kind of natural filtration, is generally preferable to the water of rivers or lakes, which being fed to a great extent by surface drainage, are therefore the receptacles of much suspended impurity, and generally yield water which is turbid.

So far as dissolved substance is concerned, those kinds of water which contain the smallest amount are generally preferable for most purposes. But the quality of water, as regards its technical and economic applications, is, within certain limits, much more influenced by the chemical nature of the dissolved contents, than by the actual amount. Those kinds of water which contain but a small amount of saline contents, or in which the saline contents, though in large amount, consist chiefly of alkaline salts, are, in ordinary language, termed "soft." Such water dissolves common soap without causing any, or at most but very little, change. On the contrary, water containing calcareous or magnesian salts in solution, decomposes soap, forming with its fatty acids insoluble compounds which separate as a curdy white precipitate. Such water is commonly called "hard," and is more or less so in proportion to the amount of earthy salts it contains. The salts which render water hard are calcic or magnesic carbonates, sulphates, or chlorides, and as the former are held in solution chiefly by carbonic acid, the hardness due to them may be, to a great extent, removed by boiling the water, and by driving off the carbonic acid, rendering the carbonates insoluble. But the hardness due to the sulphates and chlorides is not affected by boiling. Hard water is objectionable for many purposes. Its use for washing involves considerable waste of soap, since the curdy precipitate has no detergent action. For cooking and for various manufacturing purposes also, it is inferior to soft water. When it is used for supplying steam boilers, the insoluble carbonates are deposited as a crust upon the inner surface of the boiler, especially when the water also contains calcic sulphate. This salt is deposited as the water evaporates in a crystalline state, and serves to cement together the particles of carbonate precipitated when the water is first heated.

The total amount of dissolved contents in water suitable for economic and technical purposes rarely exceeds ·5 grm., or at most, 1·0 grm. per litre, and the better kinds of water contain very much less.

The presence of *dissolved organic substance* in water has probably a much greater influence in determining its fitness for dietetic purposes than either the amount or nature of the saline contents of ordinary fresh water. This is especially the case as regards the water of wells or rivers so situated that the drainage or sewage of towns passes into them. When this takes place to any considerable extent, the natural process of purification of river-water, consisting in the oxidation and destruction of the organic substance, is not sufficient to render the water of such streams fit for domestic use near the places where the sewage of large populations, or the drainage of factories, is discharged into them (p. 1018). Water containing ·1 grm. per litre of organic substance would perhaps generally be unfit for drinking, and it may be assumed that wholesome water of good quality rarely contains more than from ·005 to ·01 grm. per litre. However, in districts where peat abounds, water which is sensibly coloured by dissolved organic substance is commonly used for drinking without any deleterious results. Probably the nature of the organic substance in water, its existence in certain conditions, or its capability of promoting the development of organic germs, may be of much greater importance as regards the wholesomeness of the water, than the actual amount of it. Substances resulting from the partial decomposition of effete vegetal or animal refuse are most likely to be directly prejudicial, and also to favour the development of organic germs, especially if they are nitrogenous, and in a state of putrefactive change (FERMENTATION and PUTREFACTION, ii. 623 *et seq* ; INFUSORIA, iii. 269). This probability is at least consistent with the known effects of such substances, and with the still unexplained connection which is believed by some authorities to exist between the prevalence of epidemic disease and the contamination of water, used for domestic purposes, with sewage or some similar impurity. (Frankland, *On the Water Supply of the Metropolis*, Proc. Roy. Inst. of Great Britain.—Simon, *Report of the Medical*

Officer of the Privy Council for 1866.—Letheby, *Report to the Sanitary Committee of the Commissioners of Sewers of the City of London*, 1867, p. 11 *et seq.*, and *Report on the Cholera Epidemic of* 1866.)

The whole subject of the influence of organic substance on the character of water, in a sanitary point of view, is, however, involved in much obscurity; but there can be no doubt that water contaminated with the refuse of towns is in every respect highly objectionable for domestic purposes. Consequently the practice of discharging sewage into rivers, which at a lower part of their course furnish the water-supply of towns, cannot be too strongly deprecated for this reason, and it is scarcely less objectionable as regards the condition of rivers, and their influence on the sanitary state of the districts along their banks. On agricultural grounds, also, the vast quantity of material possessing value as manure, which is wasted by the discharge of sewage into rivers, constitutes another very cogent reason for the discontinuance of this practice, and for the adoption of some means by which the phosphates, alkalis, and ammonia contained in the refuse of towns should be turned to useful account in augmenting the production of crops, and by which at the same time the natural purity of river-water should be so far as possible preserved. (See Excrements, ii. 613; Manure, iii. 842; Urine, v. 964.)

The relative wholesomeness of water intended for domestic use appears to be so intimately connected with the presence of organic substance, that considerably attention has lately been devoted to the methods of estimating its amount and nature. Hitherto the amount of organic substance has been estimated by evaporating the water to dryness and igniting the residue so as to burn off the organic substance, the loss of weight on ignition being taken as representing organic substance. This method, however, apart from the objection of its being indirect, cannot be depended upon, for the following reasons:

1. If the residue is dried at 100° C., before ignition, it may retain water combined chiefly with calcic and magnesic chlorides or sulphates, and a considerable part of the loss on ignition, may be due to this circumstance. A further part may be due to volatilisation of ammoniacal salts, and to the decomposition of magnesic chloride, nitrites, and nitrates.

2. If the residue is dried at from 120° to 130° C. in order to expel water, there is a risk of partially decomposing the organic substance, especially when it is in a putrescent state.

3. In converting the causticised earths into carbonates, after ignition, by means of carbonic anhydride, there may be in some cases a considerable increase of weight.

The method of adding sodic carbonate to the water before evaporating to dryness, so as to decompose ammoniacal salts, and convert calcic and magnesic chlorides and sulphates into carbonates, and to obtain a residue free from water, also gives indefinite results partly for the reasons already given, and because:

4. The organic substance may be decomposed and the products volatilised during the evaporation to dryness.

5. On ignition, certain products of the organic substance may remain in a fixed state of combination in the residue.

The errors arising from one or other of these causes may exceed the whole amount of organic substance in the water; and even if that amount could be estimated with any degree of certainty, the result would not admit of any positive inference as to the character of the water, since the organic substance might be of an entirely harmless nature. (Miller, Chem. Soc. J. xviii. 117.—Frankland, Proc. Roy. Inst. Great Britain.—Wanklyn, Chapman and Smith, Laboratory, i. 98, 114; and Chem. Soc. J. [2] v. 445, 591.)

To meet these defects, the use of potassic permanganate, so as to estimate the quantity of oxygen absorbed by the organic substance in water, has been adopted by some chemists, with the object of arriving at a more direct determination of the character of water as regards this portion of its dissolved contents. As a means of estimating the amount of organic substance, it is however totally untrustworthy, as will be seen from results obtained by Professor Frankland, contained in the table on p. 1024.

These results show that from the great differences which obtain in the behaviour of organic substances with permanganate, it evidently cannot be relied upon for establishing the absence of organic substance. Even its positive indications are not alone conclusive against the character of water, since the reduction may be caused by an organic substance which is quite innocuous. Notwithstanding these facts, however, the permanganate test may afford serviceable indications as to the actual condition of water, especially when the results obtained with it are considered in connection with certain other features of the water in question, for it may reasonably be assumed that, if the presence of putrescent organic substance in water renders it unwholesome, a substance in such a state of chemical tension would be more susceptible of oxidation by permanganate than most of the substances to which Professor Frankland's experiments relate. This special applicability of the permanganate test for indicating the presence

Substance operated upon with permanganate.	1 Amount in 1,000,000 parts of water.	2 Oxygen absorbed in 10 minutes.	3 Oxygen absorbed in 6 hours.	4 Oxygen required for complete oxidation.	Indicated amount of organic substance in 1,000,000 parts of water, calculated from No. 2.	No. 3.
Gum arabic	30	·102	·350	35·5	·082	·280
Cane sugar	30	·064	·152	33·7	·051	·111
Starch	30	·143	·302	35·5	·114	·241
Gelatin	30	·792	1·836	67·6	·634	1·469
Creatin	30	·080	·172	65·9	·064	·138
Alcohol	30	·093	·164	62·6	·074	·131
Urea	30	·092	·119	64·0	·074	·095
Hippuric acid	30	·328	·600	59·0	·262	·480
Oxalic acid	30	3·747	3·750	3·8	29·98	30·00
Sodic nitrite	30	6·910	6·913	. .	55·28	55·30

of organic substance in the state most likely to be prejudicial, is not even limited by the fact that the presence of nitrites in water would determine the reduction in the same way as organic substance: for water containing nitrites is very likely to be objectionable (see under), and moreover allowance can always be made for the reduction due to nitrites; so that whenever water causes a considerable reduction of permanganate, there is at least sufficient ground for suspecting it to be unwholesome. Hence Professor Miller and others consider that the permanganate test may render good service as an accessory test, in assisting the judgment as to the salubrity of water, though it is fallacious as a substitute for the method of incineration for estimating the amount of organic substance in water. (Miller, Journ. Chem. Soc. xviii. 117.—R. A. Smith, *Estimation of the Organic Matter in Water with reference especially to Sanitary Purposes*, London, 1865.)

The idea that the deleterious influence of organic substance on the character of water is confined to that portion of it which is nitrogenous and therefore liable to putrefaction, naturally led to the attempt to determine the character of water by estimating the amount of nitrogen in the organic substance present, on the principle of its deleterious influence being proportionate to the amount of nitrogen. (Hofmann and Blyth, *Report on the Chemical Quality of the Supply of Water to the Metropolis*, 1856, p. 5.)

A method of examining water has recently been devised by Professor Frankland upon this basis. The estimation, made in the manner described under the head of WATER, ANALYSIS OF, consists of:

1. The amount of organic carbon in the dissolved contents.
2. The total amount of combined nitrogen.
3. The amount of nitrogen existing as ammonia, nitrites, and nitrates.

The difference between the last two data gives the amount of nitrogen existing in the organic substance of the water, and that is taken to be the measure of the quality of the water, so far as organic substance is concerned. One of the objections to this method appears to be the absence of any distinction either between nitrogenous organic substances which are deleterious, or may become so by putrefaction, and others of a perfectly harmless nature, or between a putrescent substance and one which is only capable of becoming so.

The liability of putrescent organic substance in water to be decomposed, and evolve its nitrogen as ammonia during evaporation to dryness, has been adopted by Professor Wanklyn, in conjunction with Chapman and Smith, as a means of ascertaining the character of water, and of estimating the amount of deleterious organic substance it contains. The decomposition of the organic substance is promoted by adding caustic alkali and potassic permanganate to the water, and the quantity of ammonia given off on distillation is then taken as a measure of the deleterious organic substance in the water. (Chem. Soc. J. [2] v. 445, 591.)

The water of rivers and wells sometimes contains ammoniacal salts, nitrites, and nitrates. Whether these substances are in themselves injurious or not, their presence in water may frequently be regarded as indicative either of sewage contamination, or of some similar objectionable admixture with the water, since they are the products of the decomposition of nitrogenous organic materials (see EREMACAUSIS, ii. 497; NITRATES, iv. 83, 90, 99). If that decomposition is incomplete, they may be accompanied by organic substance in the most objectionable state. The presence of these substances in water is, therefore, always calculated to throw suspicion on its quality. Many of the shallow wells situated in towns, and very often near a churchyard, yield water of this kind which, singularly enough, presents characters both attractive and agreeable. Being clear, sparkling, and cool, with that fresh taste which a small proportion of nitre communicates, such water often holds a high place in popular estimation, which is strengthened by the traditional repute of the wells for yielding good water, acquired probably at a time when they were surrounded by open fields, and not fed with the drainage of densely-populated streets. (See Simon, *Reports on the Sanitary Condition of the City of London*, 1849–50, p. 64; 1852–53, p. 42.—Letheby, *Report on the Quality of the Water from the Pumps and Surface Wells of the City of London*, 1866.—R. A. Smith, *loc. cit.* p. 22.—Wanklyn, Chapman, and Smith, Laboratory, i. 252.)

Sometimes, however, water which is quite beyond any suspicion of sewage-contamination or impurity, contains nitrates—as, for instance, the water obtained from artesian wells in the chalk strata. The origin of the nitric acid in this case is not ascertained, but it has been referred to an oxidation of organic substance, ammonia, or nitrogen effected by the oxygen dissolved in the water, and taking place during the passage of the water through the water-bearing strata. (NITRATES, iv. 83.)

Professor Frankland has adopted the estimation of the amount of nitrogen present in these states of combination, as the measure of the *previous sewage-contamination* of the water—that is to say, of the sewage which has been mixed with the water, and has undergone complete decomposition into its final inorganic products. To the result thus obtained he applies a correction, to compensate for that portion of the nitrogen which might have existed as ammonia and ammonic nitrite or nitrate in rain-water, taking for this purpose the mean value, deduced from the observations of Lawes, Gilbert, and Way, of ·240 pts. nitrogen existing as nitrous and nitric acids in 1,000,000 pts. of rain-water, and ·080, the maximum quantity of nitrogen existing as ammonia in 1,000,000 pts. of river-water taken near the sources of streams. This correction of ·240 + ·080 = ·320, which—upon the assumption that average filtered London sewage contains, in 1,000,000 pts., 100 pts. of combined nitrogen—corresponds to 3,200 pts. sewage in 1,000,000 pts. of water, is probably somewhat too high, and in favour of the quality of the water, since ammonia is almost entirely abstracted from rain-water in percolating through cultivated soil. The water supplied to London from the Thames, during January and February 1868, was found to contain, on the average, ·003395 grm. per litre of nitrogen in the state of ammonia, nitrites, and nitrates, or 3·395 pts. in 1,000,000 pts. of water, so that, according to this view, the amount of previous sewage-contamination would be:—

$$30{,}750 : 3{\cdot}395 - {\cdot}320 \quad = \quad 1{,}000{,}000 : 100.$$

The result thus obtained by analysis presents a very remarkable correspondence with the calculated result obtained in a different manner. Thus the average flow of the Thames, just above the point at which the London water-supply is taken, being estimated at 800,000,000 gallons daily, and the drainage of a population of about 600,000 being discharged into the Thames above that point, at the rate of about 30 gallons per head daily, the sewage-contamination of the water, according to these data, would amount to about 22,500 pts. in 1,000,000 pts. of water.

If any of the nitrogenous organic substance, originating from this sewage, had not undergone complete oxidation, its presence in the water would be indicated by the amount of nitrogen in the organic substance contained in the water. If the nitrogenous organic substance in water could be regarded as originating solely from sewage, and the nitrogen could be accurately estimated, it would be possible to determine the *present sewage-contamination* of river-water. Thus, the amount of organic nitrogen given by Professor Frankland, as existing in the water supplied to London from the Thames during the months of January and February 1868, is, on the average, ·00045 grms. per litre, which would be equivalent to 4,500 pts. of actual sewage in 1,000,000 pts. of water, or nearly ·5 per cent. (*Weekly Returns of the Registrar-General*, xxix. 35, 69). But as this quantity is little above the average apparent error of experiment (p. 1031), such a result may be disregarded. The methods by which these estimations are made, are described under the head of WATER ANALYSIS (p. 1026).

The amount of chlorine in fresh water, existing chiefly in the form of sodic chloride, will often serve, in some degree, to indicate whether it has been contaminated with sewage or other forms of animal refuse, and also, in the case of water containing organic substance, whether that is of vegetal or animal origin. It must be remembered, however, that any inference from the presence of chlorine in water must (as in the case of nitrates) be limited by the circumstance that it is a normal constituent of the contents of most natural water, and that, in certain localities, it exists in larger amount in water than in others. As a rule, water containing as much as ·01 grm. of chlorine per litre may be suspected of being contaminated with drainage. (See R. A. Smith, *On the Examination of Water for Organic Matter*, Proc. Philos. Soc. Manch.)

The wholesomeness of water appears to be intimately connected with its state of aëration. In perfectly aërated water, the ratio of oxygen to nitrogen is as 1 : 2 by volume (pp. 1014, 1017); and as this ratio is liable to be altered by the decomposition of organic substance in the water (p. 1018), the estimation of the gaseous contents of water will often serve, in conjunction with the permanganate test, to indicate the actual character of the water, as regards organic substance. Whenever the oxygen amounts to less than one-third of the nitrogen, and the water also causes a considerable reduction of permanganate, the presence of decomposing organic substance is probable. (Miller, *loc. cit.* p. 124.)

But water which is in a normal state of aëration, and does not cause any great reduction of permanganate, may still contain organic substance, either dissolved or suspended, which is susceptible of putrefaction, and therefore capable of rendering the water unwholesome (Hofmann and Blyth, *loc. cit.* p. 5). Such water, under the influence of warmth and light, often becomes putrid, and evolves stinking gases, or presents a copious development of confervæ and other minute organisms. The capability of water to remain for some days at a temperature of about 22° C., without undergoing such change, is therefore another important point to be observed in reference to the question of wholesomeness. (Angus Smith, *loc. cit.* p. 1.)

River-water is frequently so turbid, from the presence of suspended organic substance, as to be unfit for use without undergoing filtration. This is generally effected on the large scale—sand, gravel, and similar materials being used for the purpose. By this means the amount of organic substance is to some extent reduced, and even the saline contents appear to be partially abstracted.

The most effectual method of purifying water appears to be that proposed by Dr. Clark, of adding lime-water in such proportion as to combine with the free carbonic anhydride, and thus precipitate great part of the calcic carbonate. By this means the water is rendered soft, and a considerable portion of the organic substance is removed. Unfortunately, the removal of the carbonic anhydride renders the water flat and unpalatable, and the vast mass of calcic carbonate produced constitutes a serious difficulty. The addition of alum or aluminic chloride in small amount to the water has also been proposed for separating calcic carbonate and suspended organic substance by means of the basic aluminium salt produced, and then adding sodic carbonate to ensure the separation of all the alumina. The addition of sodic silicate to water intended for the use of factories has been proposed by Buff and Versmann, so as to precipitate the calcium and magnesium as silicates, and render the water soft.

Sea-water is rendered fit for drinking on board vessels by distillation, and afterwards forcing air into the condensed water. (See *Ure's Dictionary of Arts, Manufactures, and Mines*, iii. 985.) B. H. P.

WATER ANALYSIS. The examination of natural water is most frequently required for the purpose of ascertaining its fitness for economic and technical use, sometimes also for ascertaining the character of mineral water employed for medicinal purposes, &c. The mode of operating is much the same in both cases, so far as relates to the estimation of the various constituents of the dissolved contents; but, in reference to water intended for ordinary use, several special methods of examination are adopted for estimating the degree of hardness, amount and nature of the organic substance, &c., which are not employed in the analysis of mineral water.

The specific gravity of water is best ascertained by filling a flask of known capacity (100 to 300 c.c.), and furnished with a long tubular stopper, with the water at a temperature of 15·5° C., and weighing. The specific gravity of fresh water generally differs so little from that of pure water that its determination is not a matter of much importance.

The colour of water should be observed by filling a flat-bottomed glass tube with the water, and looking down through it at a white object, beside a similar tube filled with pure water. The presence of suspended substance and minute vegetal or animal organisms is also to be noted, as well as the smell or taste, both cold and when slightly warmed.

Water is often either alkaline or acid, and to ascertain this it should be tested with very delicate litmus-paper, observing whether any change of colour produced on it, disappears or not when the paper is afterwards exposed to the air. In such cases the reaction may be due to the presence of carbonic anhydride or of ammonia. Water intended for analysis should always be put at once into stoppered glass bottles when collected, and these should be quite filled, and distinctly labelled.

Estimation of Total dissolved Solid Contents.—This is effected by evaporating a known volume of the water—from half a litre to 1 or 2 litres—nearly to dryness in a platinum-basin, which need not be large enough to contain the whole quantity at once, but can be filled up from time to time. For this purpose the water should be perfectly clear; but sometimes the separation of suspended substance cannot well be effected otherwise than by leaving the water for a long time to settle, and then it is best to evaporate the water as it is. Care must be taken to avoid any access of dust or fumes, and to guard against any loss by spirting. Water containing a large amount of gaseous contents must be very carefully heated at first, for this reason. When the water has been reduced to a very small quantity, and the dissolved contents begin to separate, the evaporation is completed in a steam-bath, and the residue thoroughly dried at 100° C., until the weight remains constant.

With mineral-water containing magnesic chloride, bromide, or iodide, which are liable to be partially decomposed during the evaporation, it is advisable to add a known quantity of pure sodic carbonate, just sufficient to render the water alkaline, and to deduct the weight from that of the dry residue. But with fresh water this loss is of comparatively little importance, and it is preferable not to use sodic carbonate, which might cause decomposition of the organic substance. (See p. 1023.)

This result is useful as a control of those obtained in estimating the several constituents of the solid contents. No very close correspondence can be expected, however, especially when the residue is dried only at 100° C., since it may then contain hydrated salts; but this is probably the best temperature to employ generally, and at any rate in the first instance.

Estimation of fixed Mineral Contents.—For this purpose the residue obtained by evaporating the water to dryness, is ignited until all the carbon of the organic substance is burnt off, and the weight noted. As earthy carbonates might be partially decomposed by this treatment, the residue is then to be covered with a saturated solution of carbonic acid, again dried, and heated to about 500° C., this operation being repeated until the weight remains constant. This result, like the previous one, is chiefly useful as a control of the other results of analysis.

Estimation of Suspended Substance.—It is often very difficult to render turbid water clear by filtration, and in such cases it is best to evaporate the water at once with the suspended substance, and to fill a large stoppered bottle of known capacity with the water, leaving it until the suspended substance has subsided; then to draw off the clear water, collect the sediment on a filter, dried and weighed at 100° C., dry it at the same temperature, and weigh, afterwards burning the filter and its contents, and weighing the residue. The weight of the suspended substance dried at 100° is then to be deducted from that of the residue left on evaporation of the water (p. 1026), and after its ignition the weight is to be deducted from that of the ignited residue of evaporation.

Estimation of Hardness.—Clark's method is based upon the fact that when pure water is mixed with a very small quantity of alcoholic solution of soap, and shaken for a few minutes, a froth is produced, which is persistent for some minutes, while, on the contrary, when the water contains calcic or magnesic salts in solution, no such froth is produced until a sufficient quantity of soap-solution has been added to decompose these salts. The quantity of soap-solution requisite to produce the froth in water containing such salts is, moreover, to such an extent proportionate to the amount of these salts in the water, that with a soap-solution of known volumetric value, the degree of hardness is indicated by the quantity requisite to produce the froth in a given quantity of water.

The hardness of water is expressed in degrees, each of which represents ·01 grm. of calcic carbonate, or its equivalent of any other calcic or magnesian salt in the litre of water.

The soap-solution is made by dissolving white curd-soap in alcohol (specific gravity =·92), and its strength is adjusted so that 100 c.c. suffice to produce the froth with 100 c.c. of a solution having 20° of hardness. This solution is prepared by dissolving ·20 grm. of pure calcic carbonate in hydrochloric acid, evaporating the solution to dryness, so as to remove all excess of acid, then dissolving it in pure water, and making up the volume to exactly 1 litre. This standard calcium-solution, of 20° of hardness, is preserved in a well-stoppered bottle. A series of other calcium-standards, varying from one degree upwards, may be made by diluting that solution, in due proportions, with pure water.

The water to be examined is measured with a pipette, guaged to deliver 100 c.c. into a stoppered bottle of about double that capacity; and the soap-solution is added to it from a graduated burette in small successive portions, the water being well shaken in the bottle after each addition. This is continued until a persistent froth appears on the surface of the water. A second experiment is then made comparatively, with the water and the standard solution to which it approximates most closely in hardness.

When the hardness of water exceeds 20°, the indications of the soap-test do not correspond with the amount of calcic and magnesic salts in the water, and in that case it should be diluted with such a volume of pure water, that its hardness is reduced to within 20°, and 100 c.c. of the mixture tested. The degree of hardness found for the mixture is multiplied by 2, 3, or 4, according to the extent to which the water has been diluted.

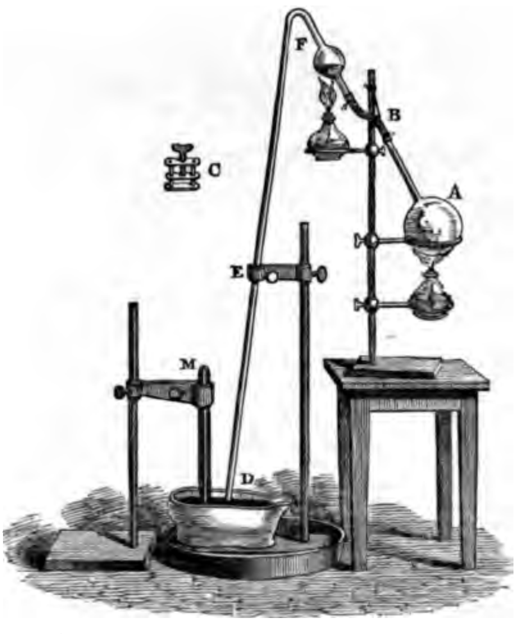
When the water contains any considerable amount of magnesic salts, the indications of the soap-test do not represent the full degree of hardness. It is therefore always necessary, after applying the soap-test, to ascertain whether magnesic salts are present, or their presence may be recognised by the curdy appearance of the water after the experiment. (Campbell, Phil. Mag. xxxvii. 171.)

After estimating the total hardness of water as above, a known quantity of the water should be boiled for an hour in a glass flask with a tube three or four feet long, resting on its neck by a bulb blown at the lower end, to serve for condensing the water-vapour. When the water is cold, some pure water is added, to make up exactly for the loss by evaporation, and the hardness is again estimated by the soap-test. It is generally found to be reduced, after the water has been boiled, in consequence of the precipitation of calcic and magnesic carbonates, originally held in solution by carbonic anhydride.

Estimation of the Carbonates precipitated by Boiling.—For this purpose the precipitate formed in the last experiment may be collected on a weighed filter, washed, dried at 100°, and weighed; any portion of the precipitate adhering to the flask may be weighed by drying the flask, weighing it, and deducting the weight of the flask. The whole of the precipitate is then dissolved by hydrochloric acid, and the calcium and the magnesium separated and estimated (iii. 753; i. 717). This precipitate may contain iron, manganese, phosphoric acid, silica, and sulphuric acid, which should be tested for and, if requisite, estimated. Sometimes, as in the analysis of fresh water, it is desirable to evaporate the water to one-half or one-fourth, before collecting the precipitate.

Estimation of the Gaseous Contents.—For this purpose a globular glass flask A (*fig.* 822) of about half a litre or a litre capacity, and having a strong piece of vulcanised caoutchouc tube B tightly fitted to its neck, is quite filled with the water to be examined, and then closed by means of a brass screw-clamp C, which presses the sides of the tube close together. The other end of the caoutchouc tube is then tightly connected with the bent glass tube D E F, having a bulb at F. This bulb is partly filled with water which is made to boil briskly, while the clamp C is still closed, and the delivery end of the tube D dips into mercury, so as to drive the air out of the tube. After the boiling has been continued for 10 or 15 minutes, until no more air escapes at D, the jar M is filled with mercury, and placed over the delivery end of the tube. The clamp C is then removed, and heat applied to the flask A, until the water boils. The boiling must be steadily kept up for fully an hour, and at last the water is made to boil briskly for a few minutes, so as to fill the delivery-tube with steam, and drive all the gas discharged from the water out of the tube into the jar M. The gas is then measured and analysed in the usual way. (ANALYSIS OF GASES, i. 268.)

Fig. 822.



Estimation of Organic Substance.—For the reasons already stated (at p. 1023), the loss of weight, caused by igniting the residue left on evaporating water to dryness, affords no adequate indication of the amount of organic substance; but it is often useful to observe the effect of heat upon this residue when igniting it (p. 1027), as a means of judging as to the amount and nature of the organic substance present, and also as to the presence of nitrates. Several methods have been proposed for the purpose of examining water for organic substance, but the one which has been most used is based upon the characteristically-marked oxidising action of potassic permanganate. Oxalic acid, dissolved in water, acidulated with sulphuric acid, is readily and completely oxidised by permanganate, yielding carbonic anhydride and water, as follows:

$$\left.\begin{matrix} \mathrm{Mn^2K^2O^8} \\ \mathrm{3\,SH^2O^4} \end{matrix}\right\} = \left\{\begin{matrix} \left.\begin{matrix}\mathrm{2\,SMnO^4} \\ \mathrm{SK^2O^4}\end{matrix}\right\} + \mathrm{3H^2O}. \\ \left.\begin{matrix} \mathrm{5\,O}\quad (80) \\ \mathrm{5\,C^2H^2O^4}\;(450)\end{matrix}\right\} = \begin{matrix}\mathrm{5\,H^2O} \\ \mathrm{10\,CO^2}.\end{matrix}\end{matrix}\right.$$

In like manner, when a few drops of a weak solution of permanganate are added to water containing organic substance and acidulated with sulphuric or hydrochloric acid, the permanganate yields oxygen to the organic substance, and the violet colour disappears. By testing the water with a permanganate-solution of known strength, it is therefore possible to ascertain how much oxygen the organic substance it contains may be capable of abstracting from permanganate.

The permanganate-solution for testing water should be of such strength that 1 c.c. will be capable of yielding exactly ·0001 grm. of oxygen (= ·0003955 crystallised permanganate). Its strength should be adjusted, immediately before using it, by means of a freshly-prepared solution of crystallised oxalic acid containing ·7875 grm. per litre. 100 c. c. of this solution, warmed with some dilute hydrochloric or sulphuric acid, should decolorise exactly 100 c.c. of the permanganate-solution.

In applying the test, a litre of the water is mixed with acid in a glass flask, and the permanganate added from a graduated burette, in small successive portions, until the water retains a very faint violet tinge, the rate of decoloration being noted meanwhile. It is then left for some minutes, and if the colour disappears, a further quantity is added, the observation being continued in this way for two or three hours or more. When the colour remains unaltered for half an hour, the volume of permanganate-solution, read off in cubic centimetres, with a small deduction for the portion which has remained unaltered, gives the quantity of oxygen absorbed, in tenths of a milligramme per litre of water. By operating in this way, some judgment may be formed as to the state of the organic substance, or some portion of it, from the rate of decoloration. (R. A. Smith, *Estimation of Organic Substance in Water*, p. 7.)

The decoloration produced during the first five or ten minutes, may be taken to represent putrescent or readily oxidisable organic substance, regard being had to the possible presence of nitrites; and a portion of the organic substance is generally found to require a much longer time for oxidation—often as much as 24 hours.

The test may also be applied by adding at once a measured excess of the permanganate-solution to the water, and leaving it for three hours, then adding a small quantity of potassic iodide-solution with some starch-paste, and estimating the quantity of iodine liberated by the excess of permanganate, with a standard solution of disodic hyposulphite containing 1 grm. of the salt per litre. The quantity of this solution required to destroy the blue tint must be read off the instant that colour disappears, as it returns after some time. The difference in cubic centimetres between the permanganate-solution added, and the hyposulphite-solution used, gives the volume of permanganate decolorised by the organic substance of the water. (Miller, Chem. Soc. J. xviii. 117.)

If the water under examination should contain nitrites, they would decolorise permanganate in the same way as organic substance; but their action is so very much more rapid than that of organic substance, that the decoloration due to them may be estimated approximatively by this difference, or still better as directed at p. 1033. For each ·001 grm. per litre of nitrous acid (NO^2), ·000348 oxygen, or 34·78 c.c. of permanganate-solution, is requisite.

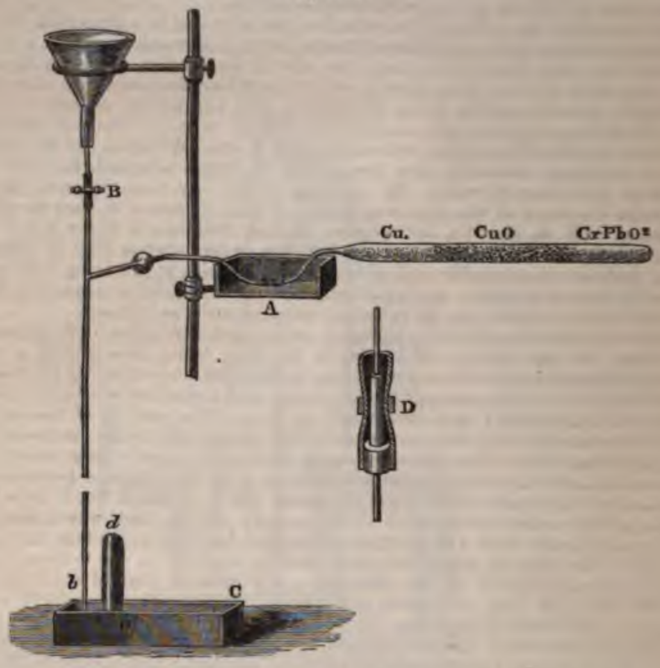
The principal defect of the permanganate test is, that it affords no certain means of distinguishing between harmless organic substance and that which may be deleterious, except in so far as putrescent substances would probably be oxidised by the permanganate most readily and most rapidly. Nor does it afford any means of distinguishing nitrogenous organic substance, which is considered to be the most prejudicial to the character of water for domestic use.

With the view of superseding the permanganate test, it has been suggested, by Frankland and Armstrong (Chem. Soc. J. xxi. 77, *et seq.*), that the carbon and nitrogen of the organic substance may be estimated by operating upon the water residue, much in the same way as the analysis of organic substances is made (i. 226 *et seq.*).

For this purpose, 1 litre of the fresh water is mixed with 30 c.c. of a fresh saturated solution of sulphurous acid, and boiled for two or three minutes. By this treatment, the carbonates are completely decomposed, and the carbonic acid expelled. Unless the water contains a considerable amount of carbonates, 2 grms. of sodic sulphite is also to be added, for ensuring the saturation of the sulphuric acids afterwards produced during the evaporation of the water to dryness. The nitrites and nitrates in the water are also decomposed, and when there is a minute quantity of iron or phosphoric acid present, every trace of nitrogen existing in those forms is separated. To ensure this result, however, it is advisable to add a few drops of ferric chloride solution to the water before evaporating it. The residue obtained from a solution of ·1 grm. potassic nitrate (=·014 grm. N) and ·1 grm. sodic chloride in pure water, treated as above described, gave, on combustion, ·00259 grm. of nitrogen; but the residues of similar solutions, to which a drop of ferric chloride had been added, gave no trace of nitrogen on combustion. Three drops of ferric chloride solution removed all trace of nitrates from half a litre of water containing 24·66 parts of nitrogen as nitrates and nitrites, in 1,000,000 pts.

After evaporating the water to dryness, at 100° C., the dry residue is mixed with a few grammes of plumbic chromate, and the whole transferred, in the usual way (i. 232), to a tube 16 inches long and sealed at one end. The tube is then charged with some granulated cupric oxide, and with bright copper turnings for about 3 inches of its length at the front part, and the open end drawn out before the blowpipe and bent downwards, so that it can be connected with a Sprengel exhaustion-pump by a piece of caoutchouc tube, and the connection immersed in a small vessel of water (as shown at A, *fig.* 823). The front part of the combustion-tube is then made hot, and the pump worked for five or ten minutes, until the air in the tube is as perfectly exhausted as possible. The calibre of the pump-tube should be 1 millimetre, and it is advisable to allow the mercury to flow very slowly, until the exhaustion is nearly complete, when a rapid stream is necessary to remove the last portion of air.

Fig. 823.



To prevent any leakage of atmospheric air into the pump, the caoutchouc pinchcock at B should be enclosed in a wide piece of vulcanised tube, and the clamp placed outside this, while the annular space between the two tubes is filled with glycerin, so that the pinchcock is entirely immersed in this liquid. With this arrangement, which is shown on a larger scale at D, the vacuum remains perfect for several days.

A tube *d*, filled with mercury, is then placed over the bent end *b*, of the pump in the mercury trough C, to collect the gaseous products; and the combustion is conducted in the usual way (i. 233), care being taken that it proceeds very slowly at first, otherwise a small quantity of carbonic oxide might be formed. The operation usually lasts nearly an hour, and at its conclusion no gas will have passed into the tube *d*, unless the water residue contained much organic substance. The pump is then set to work again for five or ten minutes, to transfer the gas into the tube *d*. This gas, consisting of carbonic anhydride, nitric oxide, and nitrogen, is analysed in the usual way (ANALYSIS OF GASES, i. 268). By this method, ·0000005 grm. carbon, and ·000001 grm. nitrogen, are stated to be distinctly measurable quantities.

The quantities of gases thus obtained represent the carbon and nitrogen of the organic substance contained in a litre of the water, and any nitrogen present in the water as ammonia. As the amount of ammonia is estimated separately, the quantity of nitrogen corresponding to it can be deducted from the total quantity.

The accuracy of the results obtained by this method evidently depends, in a great measure, upon the perfect removal of air from the tube by the Sprengel pump; and to ascertain the extent to which this can be done, two combustions were made with ·01 grm. sugar, and the quantity of nitrogen found was ·019 c.c., and ·013 c.c. at 0° C. and 760 mm. pressure, corresponding to ·000024 and ·000016 grm. of nitrogen, or ·024 and ·016 parts in 1,000,000 parts of water.

The correction to be made for the error thus arising from imperfect exhaustion, is comprised in another correction for errors of manipulation and apparatus, the amount of which is to be ascertained by making several blank experiments, in which a litre of pure water mixed with 15 c. c. of sulphurous acid solution, and about 1 grm. of recently ignited sodic chloride, is evaporated to dryness, and a combustion made with the residue, as above described. The mean quantities of carbon and nitrogen found in these experiments, are to be deducted from those obtained in the combustion of water residues. In order to reduce these errors to a minimum, it is of the utmost importance to ensure the purity of the cupric oxide and plumbic chromate, &c. used in the operation, and to guard against any access of dust or organic substance to them, or to the water, during any stage of the operation.

To show the extent to which this method may be depended upon for estimating the minute quantities of carbon and nitrogen in the organic substances likely to be present in a litre of water, several experiments were made with pure water, mixed with carbonates and known quantities of sugar or urea, varying from ·01 to ·035 grm. per litre. The results obtained for carbon differed from the calculated quantities to the extent of from 1·28 to 15 per cent., the average apparent error being ·00043 grm. on the carbon; the largest difference representing 1·22, and the smallest ·06 parts of carbon in 1,000,000 parts of water, or 2·022 and ·3 parts of the organic substance. The results obtained for nitrogen differed from the calculated quantities to the extent of from ·64 to 5·83 per cent., and in one instance 25·1 per cent., the average apparent error being ·00035 grm. on the nitrogen; the largest difference representing 1·21 and ·55, and the smallest ·03 parts of nitrogen in 1,000,000 parts of water, or 2·59, 1·17, and ·13 parts of the organic substance. The quantities of nitrogen operated upon in these experiments were much larger than those found in water of moderate quality. With mixtures of pure water, calcic carbonate, and sewage, in three different proportions, the following results were obtained:

Sewage	100,000	10,000	1,000
Water	900,000	990,000	999,000
In 1,000,000 parts.			
Organic Carbon	3·02	·33	·05
„ Nitrogen, and Nitrogen of Ammonia	3·30	·33	·04

The method proposed by **Wanklyn** in conjunction with **Chapman** and **Smith** (Chem. Soc. J. xx. 445, 591), relates especially to the nitrogenous organic substance in water. It does not, any more than the combustion or the permanganate method, afford the means of estimating the actual amount of this substance; but it has the advantage of being directly applicable to the water itself, and of furnishing results in a very short time without much trouble, so that, in regard to nitrogenous organic substance, it corresponds to the soap-test as regards hardness. This method of testing the quality of water is based upon the fact that albumin and the nitrogenous substances sometimes present in water, yield a considerable portion of their nitrogen in the form of ammonia when heated with a strongly alkaline solution of potassic permanganate. For this purpose, it is necessary in the first place to separate the ammonia existing as such in the water, and to decompose any urea that may be present. The operation is conducted as follows:—

I. A litre of the water is mixed with about 2 grms. sodic carbonate in a retort, and rapidly distilled, until the distillate, collected in separate fractions of 100 c. c., no longer gives any indication of ammonia with Nessler's test. With ordinarily good water, this generally happens when about 300 c. c. has passed over, and then the distillation is stopped. The quantity of ammonia in the first 100 c.c. may be estimated as ammonia actually present in the water, and that in the remainder of the distillate as representing urea, or the whole may be estimated together (see under). The decomposition of urea by boiling with sodic carbonate appears to depend very much on the presence of such impurities as generally accompany it in urine or sewage; pure urea is very slowly and imperfectly decomposed (*loc. cit.* p. 594).

II. The portion of the water remaining in the retort is then mixed with 20 c.c. of caustic potash solution—equal parts potash and water—and again distilled. When 300 c. c. has passed over, the distillation is stopped, and the ammonia in the distillate estimated by the Nessler test.

III. About ·3 grms. of crystallised potassic permanganate is then added to the contents of the retort, and, if requisite, 100 or 200 c.c. of pure water, the distillation recommenced, and continued until 300 c.c. has come over. The ammonia in this distillate is estimated as before, and taken, together with that in the second distillate, as representing about two-thirds of the nitrogen in the albuminoïd substance present in the litre of water.

Experiments made with solutions containing from 7 to 42 pts. fresh white of egg, or from 1 to 6 pts. of dry white of egg in 1,000,000 pts. of pure water, gave, by this treatment, quantities of ammonia which corresponded with the quantities of white of egg to within 5 per cent., the average absolute error being ·000004 grm. on the calculated quantity of ammonia obtainable.

Estimation of Ammonia.—A litre of the water is mixed with 2 grms. sodic carbonate, and distilled until 100 or 200 c.c. has passed over, and the ammonia estimated in the distillate by Nessler's method.

The test-liquid for this purpose is prepared by mixing a concentrated solution of mercuric chloride with a solution of potassic iodide in 4 parts of water, until the mercuric iodide formed ceases to be dissolved on stirring the mixture; then adding potash-solution—equal parts potash and water—until the potash amounts to six times as much as the mercuric chloride, and diluting with water until the liquid contains about 25 grammes per litre of mercuric chloride. After a day or two, the liquid becomes clear and colourless, and it is then decanted off for use.

About 3 c.c. of this test-liquid is added to one-half of the distillate from the water, in a tall narrow glass jar, and if it contains no ammonia no alteration of colour is produced; but if ammonia is present, to the extent of more than ·002 per litre, the water acquires a yellowish tinge, which is deeper in proportion to the quantity of ammonia, and when this is large a precipitate is produced.

The quantity of ammonia in the distillate may be estimated, approximately, by the depth of colour, and afterwards more accurately by comparing the depth of colour produced in the other half of the distillate with that produced in an *equal volume* of a solution containing a known quantity of ammonia, as nearly as can be judged equal to that in the distillate, on adding to each *equal quantities* of the test-solution. and repeating this comparative observation with different quantities of ammonia, until the tint of the standard solution coincides with that of the distillate. For this purpose a standard solution of ammonic chloride, containing ·317 grm. (= ·1 grm. NH^3) per litre, is prepared, and kept for making the solutions for comparison, by mixing a measured quantity with pure water to the volume of 100 c.c.

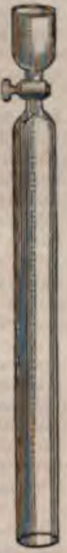
By this means very small quantities of ammonia may be estimated to within about 5 per cent. of the actual quantity. When the amount of ammonia in the water exceeds ·001 grm. per litre, the distillate must be diluted with water free from ammonia before applying the test; or the ammonia may be estimated with a standard solution of sulphuric acid (i. 190, 261).

Estimation of Nitrates and Nitrites.—The presence of nitrates or nitrites in water may be indicated by the deflagration of the residue left on evaporation, when it is ignited; or one of the tests for nitric or nitrous acids (described in iv. 83, 85) may be applied to a portion of the water evaporated to a tenth of its volume, and filtered. The amount of nitrous acid may be approximately estimated by means of permanganate-solution, especially if there is no organic substance present, or if it can be separated by mixing the water, before evaporating it, with a few drops of aluminic chloride, and then with sodic carbonate, and filtering. Each cubic centimetre of the permanganate decolorised by nitrates, represents ·0002875 grm. NO^2. The results thus obtained will always be somewhat uncertain.

Professor Frankland estimates the total amount of nitrogen present in the form of nitrates and nitrites by a method based on the reduction of the acids by mercury

(**Crum**, Phil. Mag. xxx. 426). A litre or half a litre of the water is evaporated to a small bulk, mixed with a very slight excess of argentic sulphate to convert any chlorides into sulphates, and filtered. When the water contains nitrites, they should be converted into nitrates before the evaporation, by means of permanganate-solution. The filtered liquid is then evaporated in a small beaker, to about 2 or 3 c.c., and transferred to a glass tube open at one end, and furnished with a stopcock and funnel-shaped mouth at the other end, as shown in *fig.* 824. This tube is first filled with mercury in the mercury-trough, and after the water-residue has been poured in, the beaker is rinsed first with water, and then with rather more than 3 c.c. sulphuric acid, which is also poured into the tube, care begin taken to avoid the admission of any air below the stopcock. This is then closed, and the lower end of the tube is closed, while immersed in the mercury-trough, by the thumb; so that, on removing the tube from the trough, the contents of the tube may be shaken well together, while an unbroken column of mercury, at least an inch long, remains between the acid liquid and the thumb. The evolution of nitric oxide soon begins to exert a pressure within the tube, which should be resisted; and within five minutes, when the reaction would be at an end, the gas is transferred under mercury to a suitable measuring apparatus, and the volume determined in the usual way.

Fig. 824.



To ascertain the degree of accuracy of this method, two experiments were made with ·02 and ·01 grm. of potassic nitrate; these gave quantities of nitrogen, which were ·000125 and ·000038 grm. in excess of the calculated quantities. It was ascertained that urea, creatine, uric and hippuric acid, gave no trace of gas when agitated with mercury and concentrated sulphuric acid.

Estimation of Sulphuric Acid.—A litre of the water is evaporated in a beaker to one-fourth or less, then acidulated with hydrochloric acid to dissolve any precipitate, baric chloride solution added in excess, and the precipitate collected as described at p. 537.

Estimation of Chlorine.—A litre or more of the water is evaporated to about 200 c.c., acidulated with nitric acid, and the chlorine estimated as argentic chloride, as described in i. 903.

With water containing large amounts of sulphates or chlorides, it is not necessary to operate on so much as a litre, or to evaporate the water. This may be judged of by the qualitative examination of the water.

Estimation of Carbonic Acid.—That portion of the carbonic acid which corresponds to the neutral carbonates in the water, may be estimated by evaporating a quantity of the water nearly to dryness, in a small glass flask, and treating the residue as described under the heads ACIDIMETRY and ALKALIMETRY (i. 38 and 119).

The total amount of carbonic acid in mineral-water may also be estimated by mixing a measured quantity of the water with about one-fifth of a perfectly clear solution of baric chloride and ammonia in a well-stoppered bottle, and leaving it for some days until the precipitate has perfectly subsided. The clear liquid is then decanted off, as much as possible without access of air, the bottle filled with warm water free from carbonic acid, closed, and left till the precipitate has subsided; the clear liquid is then decanted, and this operation repeated until the precipitate is sufficiently washed. It is then collected on a filter, dried, ignited, and weighed, care being taken that any portion causticised during the burning of the filter is reconverted into carbonate. The amount of carbonic acid is then estimated, either in the whole or in a portion of this precipitate, with dilute nitric acid, in an apparatus similar to *fig.* 6 (i. 119); but having a bulb blown on the tube *a b* at the upper end, while the lower end reaches only half-way into the flask, and is contracted, so that the acid contained in the bulb at *b* cannot flow out into the flask, while the wax or caoutchouc plug is in its place. After weighing the flask, the plug is loosened for an instant to let out some acid, and this is repeated from time to time until the carbonate is completely decomposed. The flask A is then placed in hot water, suction applied very gently to the tube *d*, while the plug is loosened at the same moment, and air is drawn through until the carbonic acid is entirely removed, when the apparatus is again weighed.

Estimation of Sulphuretted Hydrogen.—A litre or more of the water, acidulated with acetic acid, is mixed with some thin starch-paste in a large flask, and a solution of iodine in potassic iodide added from a graduated burette, until a persistent blue coloration is produced. The iodine-solution used for this purpose should contain ·7938 grm. per litre, and then each cubic centimetre represents ·0001 grm. sulphur.

Estimation of Iodine and Bromine.—The residue obtained by evaporating 10 or 20 litres of the water in a platinum-basin, is rubbed with alcohol of 90 per cent. until all the soluble portion is extracted. The solution is then filtered and evaporated to dryness. In the residue, iodine is estimated with palladic chloride as directed in iii. 296, and bromine as directed in i. 678.

The portion of the saline residue which is not dissolved by alcohol, may be used for estimating silica, aluminium, manganese, barium, strontium, phosphoric acid, lithium, fluorine, &c., by the methods described under these several heads. Cæsium and rubidium are tested for, and estimated, as described in i. 1113, and at p. 130 of this volume.

Boric acid is tested for by evaporating a quantity of the water to a small bulk with sodic carbonate in excess, filtering, and nearly saturating the filtrate with hydrochloric acid, then evaporating almost to dryness, separating sodic chloride by filtration, and testing the filtrate as described in i. 639.

Estimation of Silica.—The residue left after ignition of the solid contents (p. 1027), is moistened with water, mixed with excess of hydrochloric acid, and the silica separated as described at p. 245. Sometimes it is preferable to mix a litre or more of the water with a moderate excess of hydrochloric acid, and evaporate it to dryness for the estimation of silica.

Estimation of Aluminium, Iron, Manganese, and Phosphoric Acid.—The filtrate from the silica is evaporated to a small bulk in a beaker; then mixed with ammonic chloride, a slight excess of ammonia free from carbonate, and some ammonic sulphide; and kept for some hours at a gentle heat in a well covered beaker. The precipitate is collected on a filter, and washed, out of contact with air, with water containing some ammonic sulphide. The filtrate is set aside, and the precipitate, which may contain alumina, ferrous and manganous sulphides, and phosphoric acid, is either dried, ignited, and weighed, if the quantity is very small; or it is dissolved in hydrochloric acid, and the solution is boiled with a few drops of nitric acid to oxidise the sulphides. When manganese is present in any considerable amount, the solution is nearly neutralised with sodic carbonate, mixed with barytic carbonate in excess, and left for some hours in the cold. The precipitate is collected on a filter and washed, dissolved in hydrochloric acid, the barium separated with sulphuric acid, and the aluminium and iron separated as directed under IRON (iii. 387). The filtrate from the precipitate produced by barium-carbonate will contain the manganese: the barium is separated by sulphuric acid; manganese precipitated by ammonia and ammonic sulphide; and the washed precipitate is dried, ignited, and weighed. The filtrate should be tested for calcium and magnesium. When manganese is absent, or there is only a minute trace, the solution of ferrous sulphide may be at once treated with potash to separate iron and aluminium.

Estimation of Calcium and Magnesium.—The filtrate from alumina and the sulphides is mixed with a slight excess of ammonic oxalate, and the calcium estimated as directed in i. 717. Magnesium is separated from the alkaline salts with mercuric oxide as directed in iii. 753.

Estimation of Sodium and Potassium.—The filtrate from the magnesia is evaporated to dryness, and the residue weighed, then dissolved in water, and tested for sulphuric acid by adding to a portion of the liquid a few drops of alcoholic solution of strontic chloride, and some alcohol. If no precipitate appears, sulphuric acid is not present, and potassium is then separated and estimated with platinic chloride (iv. 699). If sulphuric acid is present, add some alcoholic solution of strontic chloride and some alcohol to the solution, and let it stand for some time, then collect the strontic sulphate on a filter, wash with weak alcohol, dry, ignite, and weigh. Potassium is then estimated in the filtrate with platinic chloride. By deducting from the total weight of the alkaline salts the weights of the potassic chloride and of the sodic sulphate corresponding to the sulphuric acid obtained as strontic sulphate, the quantity of sodic chloride is ascertained, and the total quantity of sodium may be calculated from these data. (See Fresenius, *Quantitative Analysis.*)

Potassium and sodium may also be estimated by evaporating a separate portion of the water to a small bulk, precipitating sulphuric acid with baric chloride, and magnesia with baryta-water, filtering, and then precipitating the excess of calcium and barium by ammonic carbonate, again filtering, and evaporating the filtrate to dryness. The residue is ignited, and dissolved in water; and when the calcium and magnesium are perfectly separated, the potassium is estimated by means of platinic chloride.

Statement of the Results of Water Analyses.—In stating the results obtained in the analysis of the contents of fresh or mineral-water, it has been customary to allocate the several acid and basic substances in various forms of combination, and, in a manner which is very much matter of individual fancy, to assume the existence in the water of certain of the salts which those substances are capable of forming. It may sometimes happen, therefore, that the statement of the same analytical results obtained by two chemists in the analysis of any particular water will, in this way, present, at first sight, an apparent diversity, which would be perplexing to those who do not understand the reason of the difference. The possibility of comparing the results of water-analyses is one of the most important requisites for all practical purposes for which they are useful. For such purposes it is of much less consequence whether certain portions of magnesium, calcium, and sodium present in water be represented as calcic and magnesic chlorides and sodic sulphate, or whether they be represented as calcic and magnesic sulphates and sodic chloride, than to be able to perceive at a glance whether, in reference to other analyses, the total amounts of the several substances present are the same or different. As regards the practical utility of such analyses, it would therefore seem desirable to avoid all hypothesis in stating their results, and to render these statements strictly comparable one with the other. This may easily be done. Thus, for instance, in the case of water containing calcic, magnesic, and sodic salts which are chlorides, sulphates, and carbonates, the simplest mode of stating the analytical results is to give the respective amounts of calcium, magnesium, sodium, chlorine, and, in the case of oxysalts, those portions of them which are equivalent to chlorine—as, for instance, sulphuric acid (SO^4) and carbonic acid (CO^3). The analyses quoted in this article are therefore stated in this manner.

The amounts of the several constituents of the solid contents are, in the case of fresh spring- and river-water, expressed as parts by weight in 1,000,000 pts. by weight of water. These data, which are in most instances sufficiently minute, are easily convertible in such form, as to correspond either with the metric system of weights and measures, or with that used in this country. Thus, for instance, in reference to fresh-water—the density of which does not differ from that of pure water to such an extent as to require notice, the litre being 1,000 grms.—these data represent milligrammes per litre of water, or grammes per cubic metre. The gallon being 10 pounds, they also represent pounds per 100,000 gallons. Thus the total solid contents of the Witley Spring-water (Table I.) amount to ·076 grm. per litre, the calcium to ·008, the magnesium to ·002 per litre, and so on, the fraction in this case being disregarded. These proportions are the same as 76, 8, and 2 grms. per cubic metre, or 76, 8, and 2 pounds per 100,000 gallons.

The data given in the tables may also be expressed as grains per gallon by multiplying with ·07. Thus the solid contents of the Witley Spring-water amount to $76 \times \cdot 07 = 5\cdot 32$ grains per gallon, the calcium to $8 \times \cdot 07 = \cdot 56$, and the magnesium to $2 \times \cdot 07 = \cdot 14$ grains per gallon. The numbers representing hardness are, in like manner, convertible into degrees of Clarke's scale by multiplying with ·7.

The data given in the table for the gaseous contents represent cubic centimetres per litre in the case of fresh spring- and river-water at the ordinary temperature of the water, and in the case of mineral-water at 0° C. and a pressure of 760 mm. These data are convertible into cubic inches per gallon, by dividing with 3·738. B. H. P.

WAVELLITE. Native phosphate of alumina, containing $3Al^2O^3.2P^2O^5.12H^2O$. (See Phosphates, iv. 551.)

WAX. This term, originally restricted to beeswax, is now extended to a class of bodies of similar character, partly of animal, partly of vegetable origin. Only a few of them have been accurately investigated. They are compounds containing but a small proportion of oxygen, and consisting of the higher members of the series of fatty acids, $C^nH^{2n}O^2$, partly free, partly in combination with alcohol-radicles; but they differ from the fats in not containing glyceryl. They are more or less hard at ordinary temperatures, softer when warmed, and melt below 100°; are insoluble in water, sparingly soluble or insoluble in alcohol, soluble in ether, volatile and fixed oils, carbonic disulphide, chloroform, &c. They are not volatile without decomposition, and burn with a bright flame when heated in the air. They are not easily saponified by boiling with potash-ley, more easily by fusion with solid potash.

1. *Animal Wax.*

The only waxes known with certainty to be of animal origin are—common beeswax; Andaquies wax (i. 291), the produce of a peculiar kind of bee found near the Oronoco and Amazon rivers; and spermaceti (p. 397). Chinese wax, or Pela, is supposed, by some authorities, to be a secretion-product of an insect, like beeswax, but it is more generally regarded as a plant-wax, exuding from *Ligustrum lucidium* and other trees, when punctured by an insect.

Beeswax. *Ordinary Wax. Cera.*—This is the substance with which bees build their cells: it was formerly supposed that the bees extracted it ready-formed from plants; but direct experiments have shown that bees fed upon pure sugar continue to produce wax, which must therefore be regarded as a true animal secretion.

Beeswax, at ordinary temperatures, is tough and solid; it has a yellow colour, a peculiar odour, and unctuous feel. When exposed, in thin shreds, to the air and sunshine, it becomes bleached, and somewhat less fusible. It may also be bleached by means of nitric acid. Chlorine likewise bleaches it, but, at the same time, forms a substitution-product, so that when candles made of wax thus bleached are burned, they give off irritating vapours of hydrochloric acid. According to A. Smith, wax may also be bleached by means of potassic bichromate and sulphuric acid.

Bleached wax contains, according to Lewy's analysis, 80·2 per cent. carbon, 13·4 hydrogen, and 6·4 oxygen. It is a mixture of three different substances, which may be separated from one another by alcohol, viz.—1. Myricin (iii. 1069), insoluble in boiling alcohol, and consisting chiefly of myricic palmitate, $C^{16}H^{31}(C^{30}H^{61})O^2$;—2. Cerotic acid, $C^{27}H^{54}O^2$ (i. 836, formerly called cerin, when obtained only in an impure state), which is dissolved by boiling alcohol, but crystallises out on cooling;—3. Cerolein (i. 836), which remains dissolved in the cold alcoholic liquid.

Beeswax is decomposed by dry distillation, giving off, first, a small quantity of water containing acetic acid, and, according to Polex, propionic acid; then a product which forms, on cooling, a white buttery mass, called wax-butter, or *Butyrum ceræ*, afterwards a more and more liquid oil, called wax-oil, still retaining a small quantity of solid matter; and finally leaves a carbonaceous mass. No acrolein is given off, but permanent gases, chiefly carbonic anhydride and ethylene, are evolved during the whole process of distillation. (Ettling.)

Wax-butter, purified by pressure from adhering oil, is mainly composed of solid hydrocarbons, cerotene, $C^{27}H^{54}$, and melissene, $C^{30}H^{60}$, together with palmitic acid. The liquid oil, when purified by rectification, consists chiefly of hydrocarbons, C^nH^{2n}; it has a specific gravity of 0·750 at 11°, and boils at 137°.

Wax, when distilled with lime, yields nearly the same products as when distilled alone. It is but slowly and incompletely saponified by potash-ley, which unites, in the first instance, with the cerotic acid; after prolonged boiling, a kind of soap is formed, which floats on water, and, when neutralised with an acid, yields myricin.

Nitric acid acts upon wax, even at a gentle heat, converting it into an oily mass, which contains pimelic, adipic, and lipic acids, and by prolonged boiling with nitric acid, yields succinic acid.—Strong *sulphuric acid* dissolves wax at 60°, the mass solidifying as it cools; at higher temperatures, carbonisation takes place.—*Chlorine* decomposes melted wax, forming chlorinated products.

2. *Vegetable Wax.*

Wax is very widely diffused in the vegetable kingdom, occurring frequently as a coating on various parts of plants—as stalks, leaves, fruits, &c.

Several of the more important plant-waxes have been already described in their alphabetical places—viz., carnauba-wax (i. 805), cork-wax or cerin (i. 837), pine-wax or ceropic acid (i. 836), sugarcane-wax or cerosin (i. 836), myrtle-wax or myrica-tallow (iii. 1069), ocuba-wax (iv. 173), and palm-wax (iv. 337).

Chinese wax, or Pela, also called *vegetable insect-wax*, or *vegetable spermaceti*, is generally supposed to be produced on certain trees by the puncture of a species of *Coccus*. It envelopes the branches as a soft white coating, about a line in thicknes, and is separated by fusion in boiling water. It consists almost wholly of cerotylic cerotate $C^{27}H^{53}(C^{27}H^{55})O^2$, contaminated only with small quantities of fatty substances. Its physical properties and most of its reactions have been already described (i. 837). When it is boiled for some time with 4 or 5 vols. of nitric acid, of specific gravity 1·40, a liquid distils over, containing butyric, œnanthylic, and caprylic acids, and in the retort there remains a liquid containing anchoic or lepargylic acid (i. 289), together with small quantities of pimelic and suberic acids.

Cowtree-wax, obtained by evaporation from the milk of the cow-tree (*Palo de Vaca, Brosimum Galactodendron*), is a waxy substance, which softens at 40°, melts at 60°, is insoluble in cold alcohol, but dissolves completely in boiling alcohol, and is saponified by alkalis. According to Berzelius, it resembles beeswax more closely than any other kind of wax. Essentially different from this wax are the resinous bodies and caoutchouc-like substance which Marchand obtained from the milk of the cow-tree. (J. pr. Chem. xxi. 43.)

Cuba-wax is a yellowish-brown wax, of unknown origin, imported from Cuba. It is softer than bees-wax, dissolves in warm ether and turpentine-oil, and almost wholly in boiling alcohol. According to Brandes, it contains 76·5 per cent. cerin, 10·5 myricin, 9·2 balsamic resin, and 3·5 water.

Japan-wax, also called *tree-wax*, and improperly *American wax*, is obtained in the East Indies from the root of *Rhus succedanea*. It is yellowish-white, of about the consistence of bleached beeswax, but somewhat softer and more friable; insoluble in water, slightly soluble in absolute alcohol at ordinary temperatures, completely at the boiling heat, soluble in ether and in volatile and fixed oils. Different samples melt at

42° to 53° or 55°. It is not a true wax, but a glyceride, being resolved by fusion with potassium-hydrate into palmitic acid and glycerin. By dry distillation, it yields palmitic acid and acrolein, a product never obtained from the true waxes. By prolonged boiling with nitric acid, it yields succinic acid.

Stop-wax, or Propolis, is the waxy substance with which bees cover over the cracks in their combs. Boiling alcohol extracts resin from it, leaving a substance called propolin, which melts at 57–58°, emitting an odour of honey. (Pellerin, J. Pharm. viii. 433.)

WAX, FOSSIL. Syn. with OZOCERITE (iv. 322).

WAX-BUTTER.
WAX-OIL. } See WAX (p. 1036).

WEBSTERITE. Native tribasic sulphate of aluminium, $3Al^2O^3.SO^3.9H^2O$, also called aluminite. (See SULPHATES, p. 579.)

WEHRLITE. A massive granular mineral, from Syurraskö in Hungary, resembling lievrite, and containing 34·6 per cent. silica, 0·12 alumina, 42·38 ferric oxide, 15·78 ferrous oxide, 0·28 manganous oxide, 5·84 lime, and 1·00 water, agreeing nearly with the formula $\left.\begin{matrix}\frac{2}{3}FeO\\ \frac{1}{3}CaO\end{matrix}\right\}SiO^2.(Fe^2O^3.SiO^2)$. Before the blowpipe it melts on the edges only; acids decompose it with difficulty. (Wehrle, Leonh. N. Jahrb. 1834, p. 627.)

WEISSIGITE. This name was given by Jenzsch to small felspathic monoclinic crystals, from the almond-stone of Weissig in Saxony, apparently identical with orthoclase (Jahresb. 1853, p. 803; 1854, p. 829; 1855, p. 947).

WEISSITE. A hydrated dichroïte, resembling fahlunite, from Fahlun in Sweden (Trolle-Wachtmeister, Pogg. Ann. xiii. 371; xiv. 190), and Potton in Upper Canada (J. pr. Chem. xiv. 35):

	SiO^2.	Al^2O^3.	FeO.	MnO.	MgO.	CaO.	K^2O.	Na^2O.	H^2O.	
Fahlun	59·69	21·70	1·43	0·63	8·99	0·30	4·10	0·68	3·20	= 100·72
Canada	55·05	22·60	12·60	. .	5·70	1·40	. .	. .	2·25	= 99·60

WELD: *Reseda Luteola.* (*Dyer's Weed. Gaude. Wau.*)—A biennial plant growing wild in many places, especially on chalky soils, and cultivated for use in dyeing. It contains a yellow colouring-matter called luteolin (iii. 736), and is much used for dyeing silk a golden-yellow, and in paper-staining.

WELTER'S BITTER. Syn. with PICRIC ACID (iv. 400).

WERNERITE. Syn. with SCAPOLITE (p. 203).

WHEAT. See CEREALS (i. 823);—also a paper, by Lawes and Gilbert, *On some Points in the Composition of Wheat-grain, its Products in the Mill, and Bread.* (Chem. Soc. Qu. J. x. 1.)

WHEWELLITE. Monoclinic crystals, observed by Brooke on a specimen of calcspar of unknown origin, and consisting, according to Sandall (Phil. Mag. xvi. 449), of calcic oxalate, ($C^2CaO^4.H^2O$?)

WHISKY. Spirit obtained by distilling the fermented wort of corn, sugar, or molasses, but generally the former.

WHITE ANTIMONY. Native antimonious oxide, Sb^2O^3; syn. with VALENTINITE (i. 323).

WHITE ARSENIC. Arsenious oxide, As^2O^3 (i. 373).

WHITE COPPERAS. Native ferric sulphate, $Fe^2(SO^4)^3.9H^2O$, also called Coquimbite (p. 595).

WHITE IRON PYRITES. The trimetric form of native disulphide of iron, FeS^2, also called MARCASITE (iii. 402).

WHITE LEAD. Amorphous basic carbonate of lead, used as a pigment (i. 786).

WHITE-LEAD ORE. Native carbonate of lead, $PbCO^3$.

WHITE PIGMENTS, The white pigment most in use is white lead: it surpasses all others in "body" or opacity, but has the defect of turning black when exposed to an atmosphere containing sulphuretted hydrogen. Sulphate of barium and oxide of zinc are free from this inconvenience; the latter is extensively used as an artist's colour, both for oil- and water-painting. Mixtures of white lead and barium-sulphate are often used in house-painting. Levigated chalk, known in France by the names *blanc d'Espagne, blanc de Meudon, blanc de Bougival, blanc de Troyes ou de Champagne,* according to the locality from which it is obtained, is also employed as a white pigment, but appears to have been used in ancient times much more extensively than at present.

WHITE TELLURIUM. Sylvanite, containing lead and antimony (p. 647).

WHITE VITRIOL. Sulphate of zinc (p. 617).

WHITNEYITE. An arsenide of copper from Houghton County, Michigan; massive, reddish-white; of specific gravity 8·408. Melts easily before the blowpipe, giving off arsenic vapours. Dissolves in nitric acid. Contains, according to Genth (Sill. Am. J. [2], xxvii. 400), 11·61 per cent. arsenic, 88·13 copper, and 0·40 silver and insoluble matter, agreeing with the formula $Cu^{18}As^2$.

WICHTISITE, WIHTISITE, or **WICHTYN.** A silicate from Wihtis in Finland; amorphous; specific gravity = 3·00. Melts before the blowpipe to a black enamel, and is not attacked by acids. Analyses: *a* by Laurent (Ann. Ch. Phys. [2], lix. 109); *b* by Strömborg (Arppe, Analyser af. finska Min. p. 17):

	SiO^2.	Al^2O^3.	Fe^2O^3.	FeO.	MnO.	CaO.	MgO.	Na^2O.		
a.	56·3	13·3	4·0	13·0	. .	6·0	3·0	3·5	=	99·1
b.	54·24	14·27	. .	15·62	2·70	5·65	3·86	3·88	=	100·22

WILLEMITE, WILHELMITE, or **WILLIAMSITE.** Anhydrous orthosilicate of zinc, $\overset{\prime\prime}{Zn}{}^2SiO^4$, or $2ZnO.SiO^2$, occurring in crystals and massive at Franklin, New Jersey, and on the Buchsbach Berg, near Aachen. The crystals are combinations of a rhombohedron with a hexagonal prism. Length of principal axis = 0·685. Angle R : R (terminal) = 115°; oR : R = 141° 39·5′. Cleavage distinct, lateral, and basal. Hardness = 5·5. Specific gravity = 3·935—4·18. Whitish or greenish-yellow, or greyish-white with rather weak vitreo-resinous lustre. Streak uncoloured. Transparent to opaque. Brittle. Fracture conchoïdal. Contains, when pure, 27·54 per cent. silica, and 72·46 zinc-oxide.

A variety called troostite from Sterling, New Jersey, has the zinc partly replaced by iron and manganese, the ferrous and manganous oxide together amounting to about 9 per cent.

WILLIAMSITE. Syn. with WILLEMITE. The name is also applied to a grey, laminar, non-aluminous serpentine, from Westchester, Pennsylvania (p. 237).

WILLOW. The inorganic constituents of the leaves, wood, and bark of *Salix vitellina* have been examined by Reichardt (Arch. Pharm. [2], lxxiii. 257; Jahresb. 1853, pp. 581–585), with especial reference to the variations in their total amount and relative proportions in spring and autumn.

WILSONITE. A silicate from Bathurst in Canada, occurring in monoclinic forms, with rose-red colour; specific gravity = 2·76—2·77; hardness very unequal in different parts. Becomes colourless and gives off water when heated, and melts with intumescence, before the blowpipe, to a white enamel. Contains, according to T. S. Hunt (*Geol. Survey of Canada*, 1853), 43·55 per cent. silica, 27·94 alumina, 0·20 ferric and manganic oxides, 6·50 lime, 3·81 magnesia, 1·45 soda, 8·37 potash, and 8·61 water (= 100·43).

WILUITE. A variety of lime-garnet, also called *grossularia* (see GARNET, ii. 772). The same name is sometimes applied to vesuvian (p. 998).

WIND-FURNACE, or **AIR-FURNACE.** The ordinary furnace used for crucible operations, in which the draught is produced, without the aid of a blast, by the difference of specific gravity of the heated air in the chimney and the external air.

WINE. Synonyms: *Wein. Vin. Vinum.* Οἶνος.—This name is applied, in a general sense, to all alcoholic liquors produced by fermentation of saccharine juices of plants (FERMENTATION, ALCOHOLIC, ii. 628), but it is more usually restricted to the fermented juice of the grapes of *Vitis vinifera.*

The chief constituent of wine, besides water, is alcohol, the amount varying from 6 to 17 per cent. in different kinds of wine, as shown in the following table. The quality and value of wine is, however, determined much less by the amount of alcohol it contains, than by the flavour and bouquet which it possesses. These characters, which are due to the presence, in very minute proportions, of ethereal and aromatic substances, differ in kind in different sorts of wine, and in degree in the same kind of wine. The chemical nature of the substances which constitute the bouquet of different wines is as yet but little known. They are produced, partly during the fermentation of the grape-juice, and chiefly by the mutual reaction of various constituents, when new wine is kept (Berthelot, Compt. rend. lvii. 287, 398, and 795.—Pasteur, *ibid.* p. 936):—

	Alcohol. Percentage by weight.	Extract.	Acid.	Sugar.	Authority.
Port, old	20·29	5·80	·36	3·31	Griffin
Port { Maximum	17·10	. .	. .	. .	Christison
Mean of 7 samples	16·20				
Minimum	14·97				
Sherry { Maximum	16·17				
Mean of 13 samples	15·37				
„ „ 9 old samples	14·72				
Minimum	13·98				
Montilla, 1854	16·62	2·49	·43	·60	Griffin
Madeira	16·90	. .	. .	. .	Christison
Amontillado	12·63				
Chateau Latour, 1825	7·78				
Claret	8·99				
St. Julien, 1858	9·84	2·67	·65	·25	Griffin
Rudesheimer	8·40	. .	. .	. .	Christison
„	13·32	2·84	·63	·17	Griffin
Steinberger, 1846	10·17	10·5	·424	. .	Fresenius
Markobrunner, 1846	11·14	5·5	·533		

It is stated that in wines imported into England, especially port and sherry, the amount of alcohol is habitually augmented by mixing them with brandy. Natural wine made from grape-juice containing 20 per cent. of glucose should not contain much more than 10 per cent. by weight of alcohol, unless it has been long kept in casks, and there has been a considerable separation of water by evaporation through the wood, and a consequent increase in the amount of alcohol. But if the wine of hot countries is produced from grape-juice containing 30 per cent. of sugar, it might well contain 16 or 17 per cent. of alcohol after being kept in casks.

The peculiar smell which is common to all wine is probably due to the presence of an ether, which Liebig and Pelouze have termed œnanthic ether (iv. 174).

Some kinds of wine, such as Malaga, Tokay, Tent, and Frontignac, contain a considerable amount of sugar; others, like Rhine wine, Bordeaux, and Burgundy, are almost destitute of sugar. The sweetness of wine may, in some cases, be due to the presence of glycerin, which appears to be a product of fermentation (ii. 628).

All kinds of wine contain free acid, which is partly tartaric acid, perhaps also succinic, malic, and citric acids, together with tannic and gallic acids, and acid potassic tartrate.

The colour of wine is chiefly derived from the husks of the grapes, especially in the case of red wine. White wine frequently derives a portion of its colour from the oak-casks in which it is kept. The chemical nature of the substances to which the colour of wine is due is but little known (Fauré, *Analyse chim. et comparée des Vins, &c.*—Batilliat, *Traité sur les Vins de la France.*)

On evaporating wine to dryness at 100° C., it leaves an extract, which varies from 2 to 5 per cent., and sometimes amounts to 10 per cent. and upwards. The amount is less in dry wines than in sweet wine, and it decreases as the wine is kept.

Wine is often liable to undergo certain changes, which render it unfit for use, sometimes becoming turbid or ropy. These effects are chiefly referable to the presence of ferment, or of nitrogenous substance capable of conversion into ferment, and they result from imperfections in the manufacture. Pasteur (Compt. rend. lx. 899, 1109; lxi. 274) recommends heating the wine in closed bottles to about 60° C., for an hour or two, in order to prevent these changes.

Effervescent wines contain carbonic anhydride dissolved under pressure, and resulting from fermentation, produced after bottling the wine by adding to it a solution of sugar.

For analyses of wine see Fontenelle, J. Chim. Méd. iii. 332.—Payen, *Chim. indust.*—Pelouze and Frémy, *Traité*, iii. 436.—Malland, J. Chim. Méd. iii. 326. —Fauré, J. Pharm. vii. 200.—Brande, Phil. Trans. 1811.—Bouis, Brandes Archiv. xxv. 222.—Christison, Edinb. Phil. Journ. 1838.—Khol, J. Chim. Méd. [4], ii. 251.—Ludersdorf, J. pr. Chem. xxiv. 102.—Geiger, Mag. f. Pharm. xix. 266.—Fischern, Ann. Ch. Pharm. lviii. 705.—Fresenius, Ann. Ch. Pharm. lxiii. 384.—Beck, Edinb. Phil. Journ. 1835.—Diez, Ann. Ch. Pharm. xcvi. 304.—Zierl, Baierisch. Kunst. Gewerbeblatt, 1838.—Soubeiran, *Traité de Pharmacie*, i. 129.—

Schubert, Pogg. Ann. lxx. 397.—Kersting, Ann. Ch. Pharm. lxx. 250.—Geromont, Ann. Ch. Pharm. xvii. 158.—Mitis, Baierisch. K. Gewerbeblatt, 1838.—Hitchcock, Edinb. Phil. Journ. xxxvii. 176.—Griffin, *Chemical Testing of Wines and Spirits*, p. 10.—Mulder, *Chemistry of Wine.*

Manufacture of Wine.—The grapes grown in wine-producing countries generally consist, when ripe, of from 70 to 75 per cent. juice, 20 to 25 per cent. moist skins and stones, and from 3 to 5 per cent. of stalks. The skins are covered with a whitish pulverulent bloom, consisting of a waxy substance. They consist chiefly of compact cellular tissue containing nitrogenous substances, fat, &c., with an internal layer of vegetable tissue containing nitrogenous and colouring-matters, essential oil, tannin, and salts. The fleshy part of the grape consists of cells and vessels, which contain the chief part of the juice. The stones consist chiefly of cellulose, and contain also fatty and ethereal oils, nitrogenous substance, and tannin. The stalks contain acids, tannin, chlorophyll, and similar substances, but scarcely a trace of glucose. The constituents of the juice are chiefly water and glucose, together with gum, pectin, dissolved and suspended nitrogenous substances, tartaric acid—perhaps also racemic acid, malic acid,[*] citric acid,[†] paracitric acid, succinic acid, and acetic acid,[‡] partly free and partly as salts. It also contains fatty and ethereal oils, wax and resin, colour-substance, tannin, phosphates, sulphates, and other mineral substances in small amounts.

Composition of Grapes.

	Ripe white Austrian grapes.	Kleinberger grapes,		Riesling grapes, very ripe.	Johannisberg grapes.	Assmannshauser grapes.
		ripe.	very ripe.			
	Fresenius.	*Schlieper.*		*Fresenius.*	*Fresenius.*	
Glucose . . .	13·8	10·6	13·5	15·1	19·2	17·3
Tartaric acid . .	1·11	·92	·78	·56	·74	·84
Albuminoïd Substance . . .	·8	·6	4·1	3·4	3·0	
Pectin, Gum, Fat, &c.	·5	·2				
Ash	·36	·38				
Soluble portion . .	16·5	12·6	18	19·1	22·9	
Water . . .	79·8	84·9	76·3	74·4		
Skins, Stones, and Cellulose . .	2·6	1·8	·0			
Pectose . . .	·9	·7				
Ash . . .	·11	·08				
Insoluble portion .	3·53	2·52	5·66	6·52		

The amount of glucose in grape-juice varies from 10 to 30 per cent., according to the climate and season in which the grapes grow; and the amount of free acid, considered as tartaric acid, varies, under the same conditions, from ·3 to 1·5 per cent. The juice of grapes used for making wine is generally colourless, or very slightly yellowish, and it is almost without odour, except that of the Muscat grape. With the exception also of the *teinturier* grape, which has coloured pulp, the yellow and blue colouring substances of grapes are contained in their skins. They are closely analogous to tannin, and are more soluble in alcohol containing acid than in water.

In regard to the production of wine, the principal constituents of grape-juice are glucose, the acids, and the nitrogenous substances which furnish the ferment, so that the raw material for the production of wine may be regarded as a solution of glucose in water, containing also those substances.

It is especially important that the grapes used for making wine should be allowed, as far as possible, to attain full maturity, and become perfectly ripe, in order that there may be a maximum amount of glucose, and a minimum amount of free acid, in the juice (FRUIT, ii. 710, 711). Immediately after the grapes have been gathered, they are crushed, either in vats or between wooden rollers. In some places they are first picked from the stalks, in other places they are pressed together with the stalks. The juice is then either separated at once from the husks and stones, &c., by pressing the crushed grapes, and the expressed juice, or "must," is left in vats to ferment without the "marc"; or the crushed grapes are first allowed to ferment for some time with the husks, as in the manufacture of red wine, and the marc is separated after the fermentation, when sufficient colour has been extracted. During the first stage of the fermentation, the temperature of the liquid rises, and as the conversion of glucose into alcohol progresses, some acid potassic tartrate is deposited (p. 678), together with portions of the ferment and other organic substances, forming what is termed "lees." As the evolution of carbonic anhydride subsides, the liquid gradually becomes clearer. This stage of the fermentation is sometimes at an end within two or three days, but it sometimes lasts much longer. In order to prevent the production of acetic acid by oxidation of alcohol, it is generally customary to draw off the fermented liquor from the lees, as soon as the evolution of gas has become comparatively scanty, and to transfer it to casks in which the fermentation continues slowly, for a considerable time longer, acid potassic tartrate being deposited meanwhile as a crystalline crust on the sides of the casks (TARTAR, p. 671). After a time, when the production of alcohol is at an end, the wine is again transferred to other casks, and is kept for a long time, during which its constituents undergo those changes by which it chiefly acquires flavour, bouquet, and ripeness. In this way what is termed "natural wine" is produced.

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[*] Pasteur, J. Pharm. [3], xxiv. 75.—Schwartz, Ann. Ch. Pharm. lxxxiv. 83.

[†] Winckler, Jahrb. Pharm. i. 57.

[‡] Berthelot and Fleurieu, Compt. rend. lvii. 397.

During the first stage of the fermentation, which is essentially analogous to that of beer-wort (i. 529), the greater part of the glucose is converted into alcohol, and much of the nitrogenous substance which yields the ferment is separated. The amount of glucose remaining unaltered, depends partly on the amount originally contained in the "must," and partly on the temperature at which the fermentation takes place. At a temperature of 10° C., fermentation ceases when the alcohol produced amounts to 10·5 or 11 per cent. by weight, but at a higher temperature, it may continue until the alcohol amounts to 13 per cent. or more. During the second stage of the fermentation, when the weather has become cooler, there is less fear of alcohol being oxidised, and the moderate access of air to the wine has chiefly the effect of causing the ferment to separate from it.

Hitherto little attention has been paid to the regulation of the temperature at which the fermentation takes place, and although it is highly probable that the quality of wine depends very much upon this circumstance, it is almost entirely a matter of local accident, whether the fermentation takes place at a high or low temperature. Active fermentation at a high temperature, is calculated to furnish wine which is free from sugar, and soon becomes ready for use; but the wine thus produced, like much of the Italian and Hungarian wine, has generally little or no bouquet or flavour, and is not capable of being kept long. On the contrary, slow fermentation at a low temperature, furnishes wine which not only keeps better, but acquires eventually a finer bouquet, and becomes generally of better quality than that produced by more rapid fermentation at a higher temperature. In the Moselle and Rhine districts, the fermentation is conducted at a time of year when the weather is much colder than it is in Italy, and even there, the wine produced in seasons which, from their warmth, are especially favourable to the growth and maturation of the grapes, and continue warm until late in the year, is not always so good as that of years when the autumn is colder.

The character of wine also depends very largely on the composition of the "must" from which it has been produced, especially on the amounts of glucose and of acid which the must contained, and on the relative proportions of these substances. Generally speaking, in southern countries, where the amount of sugar in the grape-juice is largest, as in Greece, Portugal and Spain, the wine produced contains a large amount of alcohol, some unfermented sugar, and but little bouquet as compared with the wine of northern countries, such as that of the Moselle and Rhine districts, which contains less alcohol, no sugar, and a larger amount of acid, but is chiefly characterised by its fine aroma. The grape-juice of these countries generally contains a smaller amount of sugar, and a much larger proportion of acid, than that of southern countries. But besides the differences due to climate, variations of season also exercise a further influence of a similar nature, especially in the northern wine-producing districts, where in cold seasons the amount of sugar is small, while the proportion of acid to sugar in the grape-juice is frequently twice as great as it is in more favourable years, and consequently the wine produced there is only occasionally good, and very often can scarcely be drunk.

To produce good wine, it is essential that the grape-juice should contain at least 20 per cent. of glucose, and that with this amount it should not contain more than ·5 per cent. of acid. These conditions do not always obtain. In the Moselle district, for instance, the proportion of acid to glucose is often as 1 to 12, while the amount of glucose is also very small. In such cases the wine made from natural grape-juice is necessarily inferior; but it is possible to remedy these natural defects of the grape, and by doing so, to render it capable of producing better wine, especially in unfavourable years. With this object, several methods have been proposed, of which the following are among the principal:—

1. Concentrating the grape-juice by partially drying the grapes before they are crushed, or by evaporating the "must."—This method is practised in some parts of Hungary, Spain, Italy, and France, but it has only a limited applicability, and is more adapted to the production of liqueur wines than for improving the quality of wine when the grape contains little sugar and much acid.

2. Adding glucose to the must when it amounts to less than 20 per cent.—This method only partially rectifies the natural defects of the grape-juice, and although it would furnish a wine containing more spirit than that produced from the unmixed must, the excessive amount of acid is not affected except in so far as it may be masked by an excess of sugar.

3. Diluting the must with water sufficient to reduce the amount of acid to ·5 per cent., and then adding glucose until this amounts to 20 per cent. in the must.—The adoption of this method was at first strongly opposed on the ground that wine thus prepared, might be expected to be deficient in flavour and bouquet; but this has been found not to be the case, and the result is quite consistent with the fact that the flavour and bouquet of wine are produced during the fermentation. So far as the product of fermentation is concerned, it is therefore a matter of little consequence whether the glucose has been derived from the grape, or from some other source, provided the grape-juice contains a sufficient amount of ferment, acid, and other substances, requisite for the production of good wine, and these are generally present in excess. The principal condition to be ensured is the purity of the glucose employed.

4. Mixing the pressed grape marc with water containing 20 per cent. of glucose, and fermenting.—This method is based on the important observation, that the marc from which the grape-juice has been expressed, still contains a large amount of those substances, which by fermentation with a solution of glucose, communicate to it the characters of wine, and are capable, under the influence of this process, of yielding the products which constitute the bouquet, etc. (Pétiot, Bulletin soc. d'Encour., 1857, p. 559). The wine prepared by this method, is stated to be even better than that obtained from the grape-juice itself.

These last two methods bear the character of rational improvements in the manufacture of wine, and are in this respect to be regarded as totally different from that system of compounding, justly termed adulteration, which has been practised with the object of giving inferior wine the semblance of character it can acquire only by the process of fermentation, and in the highest degree, only in certain favourable years. Pasteur's method of maturing wine by the application of heat instead of keeping it for a number of years, is likewise an improvement which is sound in principle, and likely to be of considerable advantage. The chemistry of wine is, however, still so imperfectly understood, both as regards its composition and its production, that the methods above referred to must be regarded merely as first steps towards real improvement in the practice of an art which has hitherto been conducted in a most crude and empirical manner, subject to the accidental influence of conditions whose operation and effects were wholly unknown, and regulated by the most fantastic notions.

Analysis of Wine.—The chief data, &c. determined for practical purposes, are:—

1. The amount of *alcohol*; 2. The amount of *free acid*; and 3. The amount of non-volatile dissolved contents, or "*extract*," as it is termed. Neither the flavour nor the bouquet of wine are susceptible of estimation by chemical means. The colouring substances of wine are also too little known to be distinguished with certainty from other colouring substances employed for its adulteration. (Blume, Dingler's Journ. clxx. 240.)

Estimation of Alcohol.—The most trustworthy method consists in distilling out the alcohol as already described under the head of BEER (i. 530), and weighing or observing the density of the distillate (ALCOHOLOMETRY, i. 81). The free acid in the wine should be first neutralised by sodic carbonate or baryta-water, and a very small quantity of tannic acid added to prevent the wine from frothing when distilled. The percentage of absolute alcohol should be expressed by weight, that of proof-spirit by volume.

Estimation of Free Acid.—This may be effected with a standard solution of alkali, as described under ACIDIMETRY (i. 262).

The amount of acid potassic tartrate may be estimated by mixing the wine with five times its volume of mixed alcohol and ether (equal parts) and leaving it for twenty-four hours, when the salt will have deposited almost entirely. (Berthelot and Fleurien, Compt. rend. lvii. 394.)

If it be desirable to ascertain the relative proportions of fixed and volatile acids in wine, this may be done approximately by distilling the wine and estimating the quantity of acid in the distillate; but the result obtained will not represent the full amount of free volatile acid, and cannot be much relied upon.

Estimation of "Extract."—This is made in the same manner as with BEER (i. 530). If the amount is considerable, it may be desirable to ascertain what it consists of.

Estimation of Sugar.—This may be made by one of the methods described under SACCHARIMETRY (p. 371). It is necessary, in using the copper-method, first to separate the colouring substance of the wine. When the fermentation method is adopted, the alcohol in the wine should be first distilled off, and the result obtained by weighing the carbonic acid as barium-carbonate may be checked by estimating the alcohol produced.

The inorganic constituents of wine may be estimated by igniting the residue left on evaporation. The amount of potash thus found may be taken as representing the acid potassic tartrate in the wine.

For more detailed descriptions of the methods and apparatus to be used in the analysis of wine, see Bolley and Paul, *Manual of Technical Analysis*, p. 331, and Griffin, *Chemical Testing of Wines and Spirit;* also a paper by Dr. A. Dupré, *On the Estimation of Compound Ethers in Wine.* (Chem. Soc. J. xx. 493.) B. H. P.

WINE, OIL OF. See ETHERIN (ii. 507).

WISERITE. A hydrated carbonate of manganese, from Gonzen, near Sarganz, in the Grisons; regarded as a variety of diallogite.

WITHAMITE. A bright-red variety of epidote; the crystals exhibit a straw-yellow in one direction across the prism.

WITHERITE. Native carbonate of barium (i. 780).

WITTICHENITE or **WITTICHITE.** Sulphide of copper and bismuth, $Cu^3Bi'''S^3$, from Wittichen in Baden (ii. 76).

WITTINGITE. A ferrico-manganic silicate, from the Wittinge iron-mine at Storkyro in Finland, containing, according to a preliminary analysis by Igelström, 33·28 per cent. silica, 5·93 ferric oxide, 51·79 manganic oxide, and 9·0 water.

WOAD. *Isatis tinctoria.* (*Guède. Pastel. Wau.*)—This plant has been used from ancient times for dyeing blue, and before the introduction of indigo was of great importance for that purpose. Schunck (Phil. Mag. [4], x. 73) has shown that the leaves of woad do not contain either indigo-blue or indigo-white, but indican (iii. 246), a compound which may be extracted from them by alcohol, and is resolved, by heating with dilute acids, into indigo-blue and indiglucin:

$$\underset{\text{Indican.}}{C^{26}H^{31}NO^{17}} + 2H^2O = \underset{\text{Indigo-blue.}}{C^8H^5NO} + \underset{\text{Indiglucin.}}{3C^6H^{10}O^6}.$$

Woad is cultivated in France, in several parts of Germany (Thuringia, Silesia, &c.), and other countries. It is sown in March, and the leaves are cut for the first time in June; later in the season, the plants yield fresh crops of leaves, but these do not contain so much colouring-matter as the first. The leaves are sometimes merely dried, and sent to market in that state; or they are ground to a paste in a mill, and the paste is made up into heaps, left for some time, and then formed into balls or loaves, which are dried and sent into commerce.

At the present day, woad is but rarely employed in dyeing, as the use of indigo is found to be much more economical; but as it easily ferments when moist, it is used for the reduction of indigo in the so-called *woad-vats.* (See INDIGO, ii. 252.)

WÖHLERITE. A silico-zirconio-niobate of calcium and sodium, occurring at the Langesundfjord, near Brevig, in Norway, in tabular crystals and prisms belonging to the trimetric system. Axes $a : b : c = 1 : 1·01583 : 0·7261$. Angle $\infty P : \infty P = 90° 54'$; $oP : \bar{P}\infty = 144° 1'$. Cleavage distinct in one direction. The mineral also occurs granular. Hardness = 5·5. Specific gravity = 3·41. Lustre vitreous, inclining to resinous. Colour light-yellow, brownish, or greyish; streak yellowish-white. Transparent to subtranslucent. Fracture more or less conchoïdal to splintery. When strongly heated before the blowpipe, it melts quietly to a yellowish glass; with fluxes, it gives the reactions of iron, manganese, and silica. Hydrochloric acid decomposes it, with separation of silicic and niobic acids. Contains, according to Scheerer (Pogg. Ann. xcii. 242), 14·47 per cent. Nb^2O^5, 15·17 ZrO^2, 30·62 SiO^2, 1·91 FeO, 1·55 MnO, 26·19 CaO, 0·40 MgO, 8·39 Na^2O, and 0·2 water (= 98·94).

WÖRTHITE. An altered or hydrous kyanite (iii. 449), from near St. Petersburg. Hardness = 7·25, white and translucent. Contains, according to Hess, (Pogg. Ann. xxi. 73), 40·58 per cent. silica, 53·50 Al^2O^3, 1·00 MgO, and 4·63 H^2O (= 99·71).

WOLCHITE. Antimonial copper-glance (ii. 76).

WOLCHONSKOÏTE. A chromiferous clay from Ochansk in Siberia, containing, according to Kersten (Pogg. Ann. xlvii. 485):

SiO^2.	Al^2O^3.	Cr^2O^3.	Fe^2O^3.	CaO.	MgO.	MnO.	H^2O.	
37·01	6·47	17·93	10·43	1·01	1·91	1·66	21·84	= 98·26

WOLFRAM. Native tungstate of manganese and iron (p. 907). The same name is also applied to metallic tungsten.

WOLFRAMINE, or **WOLFRAM-OCHRE.** Native tungstic oxide (p. 903).

WOLFSBERGITE. Native cuprous sulphantimonite, or antimonial copper, $Cu,Sb'''S^2$, or $Cu^2S.Sb^2S^3$ (ii. 76).

WOLLASTONITE. Native metasilicate of calcium, $Ca''SiO^3$ (p. 252).

WONGSHY, or **WONGSKY.** The Chinese name for the pods of *Gardenia grandiflora*, which yield a large quantity of a yellow colouring-matter, 1 pt. of wongshy being sufficient to impart a strong yellow colour to 60 pts. of water. The pods contain also pectin, mucus, tannic acid, and fat. The aqueous extract has a fiery-red colour when concentrated, yellow when dilute. The alcoholic extract is fiery-red.

The colouring-matter of wongshy has been shown by Rochleder to be identical with crocin from saffron (ii. 108).—Respecting the products obtained from it by Orth, see J. pr. Chem. lxv. 16.—Chinese yellow-pods contain 5 per cent. ash, consisting in 100 pts. of 29·2 pts. K^2O, 11·3 Na^2O, 12·0 CaO, 3·5 MgO, 5·5 Fe^2O^3, 0·9 SO^3, 10·3 P^2O^5, 4·0 SiO^2, and 0·5 Cl. (Stein, J. pr. Chem. xlviii. 329.)

The aqueous extract of wongshy colours wool and silk a fine yellow, without mordants; cotton to be dyed with it must first be mordanted, best with tin-solution. The colour withstands the action of soap; alkalis turn it more yellow, acids more reddish. The colour does not withstand the action of light, but is most permanent on silk. The colour of wongshy has a great resemblance to that of annotto.

WOOD. Respecting the chemical composition of wood, two different views are entertained. According to Payen (Compt. rend. viii. 51), v. Baumhauer (J. pr. Chem. xxxii. 204), and F. Schulze (Chem. Centr. 1857, p. 321), it consists of cellulose or woody fibre (i. 818), which forms the cell-walls, and of incrusting substances deposited thereon (*Sclerogen*, *Lignin*, formed of products of decomposition of the decaying cells [Schleiden, *Grundz. d. wiss. Botanik*, Leipzig, 1849, i. 172]). Frémy, on the other hand (Compt. rend. xlviii. 862), denies the existence of incrusting substances, and supposes that the true woody tissue consists of *vasculose*, the constituent of the vessels (p. 995), which is insoluble in oil of vitriol, soluble in boiling concentrated potash-ley; *paracellulose*, the substance of the medullary rays (iv. 34), soluble in oil of vitriol and in boiling potash-ley; and *fibrose*, the substance of the true woody fibres, soluble in oil of vitriol, but insoluble in boiling concentrated potash-ley. The former view is, however, generally regarded as the more exact. Wood likewise contains the following substances, in quantities varying with the season and locality, and with the species and age of the plant: the constituents of the sap, such as albuminoïdal substances (0·81—0·12 per cent. nitrogen, according to Chevandier), sugar, gum, tannic acid, &c., colouring-matters, starch (only in autumn and winter), pectose, according to Frémy (Payen found none), resins and volatile oils, and the ordinary mineral constituents of plants.

The external properties of wood depend, partly on the mode of union of the fibres, partly on the proportions between the essential or adventitious proximate constituents. Hence the several species of wood differ greatly in hardness, colour, and apparent specific gravity. The latter, that is to say, the specific gravity of the wood air-dried, but still *containing air*, varies, according to Karmarsch (*Gründz. d. mech. Technologie*, p. 635), from 0·383 (poplar-wood) to 1·342 (logwood). The actual specific gravity of different kinds of wood is tolerably uniform: 1·5, according to Violette; from 1·46 (maple) to 1·53 (oak), according to Rumford. Wood always contains a larger quantity of carbon than cellulose; its composition varies between very wide limits (according to the nature of the incrusting substances: Payen), as much apparently in the same as in different woods. The lowest and highest amounts actually found are: 46·10 per cent. carbon (beech-wood: Baer), and 54·44 per cent. (oak-wood: Payen); (beech-wood = 54·35);—5·55 per cent. hydrogen (box-wood: Prout), and 6·40 per cent. hydrogen (aspen-wood: Payen);—39·32 per cent. oxygen (oak-wood: Payen), and 46·87 per cent. (beech-wood: Baer).

Decay of Woody Fibre.—Moist wood exposed to the air, gradually undergoes decomposition, a species of fermentation being set up by the nitrogenous constituents, in consequence of which, oxygen is absorbed, carbonic acid and water are evolved, and the wood crumbles down into a blackish-brown vegetable mould, called humus, ulmin, or gein (p. 936). This decay occurs most rapidly in young spongy wood, which admits the air more freely, and at the same time contains a larger proportion of the albuminous substance than harder and older wood.

The process of decay in ligneous tissue varies considerably, according as it takes place with free access of air, or under water with but a scanty supply of oxygen from without. When the air has free access, its oxygen is converted into an equal bulk of carbonic anhydride, and at the same time a large quantity of water is evolved (Saussure). According to Hermann, a small portion of nitrogen is absorbed during the process, and ammonia is produced. The water is formed at the expense of the oxygen and hydrogen of the woody tissue, so that the mouldered products contain a larger proportion of carbon than the wood in its original state. If the moist wood is excluded from the air, a small quantity of carbonic anhydride is evolved during its decay, accompanied, as in the former case, by separation of water; and under certain circumstances, marsh-gas is liberated in considerable quantity.

Such is a general view of the changes which take place in the conversion of woody tissue into humus, peat, lignite, bituminous coal, and anthracite, the proportion of carbon in these successive products of transformation continually increasing, until in the last the carbon is found associated with only small quantities of hydrogen and oxygen. (See Table of the Composition of Wood and Coal, given under COAL, i. 1030, 1031.)

The composition of wood (oak) given in the table may be approximately represented by the empirical formula $C^{34}H^{48}O^{22}$; that of certain kinds of peat by $C^{20}H^{22}O^{8}$; that of Bovey lignite by $C^{27}H^{28}O^{7}$; that of Wigan cannel-coal by $C^{26}H^{20}O^{2}$; and that of Welsh anthracite by $C^{40}H^{16}O$. If now the woody tissue be acted upon by a small quantity of oxygen, such as might be supplied by solution in water, each of these products of transformation may be supposed to be formed by the separation of marsh-gas, carbonic anhydride, and water, in the proportions represented by the following equations:*

$$\begin{array}{llllll}
\underset{\text{Wood.}}{C^{34}H^{48}O^{22}} + O^{3} & = & \underset{\text{Peat.}}{C^{20}H^{22}O^{8}} & + 6CH^{4} & + 8CO^{2} & + H^{2}O \\
\underset{\text{Wood.}}{C^{34}H^{48}O^{22}} + O & = & \underset{\text{Lignite.}}{C^{27}H^{28}O^{7}} & + 2CH^{4} & + 5CO^{2} & + 6H^{2}O \\
\underset{\text{Wood.}}{C^{34}H^{48}O^{22}} + O^{2} & = & \underset{\text{Cannel.}}{C^{26}H^{20}O^{2}} & + 2CH^{4} & + 6CO^{2} & + 10H^{2}O \\
\underset{\text{Wood.}}{2C^{34}H^{48}O^{22}} + O^{5} & = & \underset{\text{Anthracite.}}{C^{40}H^{16}O} & + 12CH^{4} & + 16CO^{2} & + 16H^{2}O.
\end{array}$$

Destructive Distillation of Wood.—The products formed by the distillation of wood in close vessels, vary with the nature of the wood operated on, and the temperature at which the distillation is effected. The decomposition begins at about 140°. The volatile portion of the products includes permanent gases—chiefly carbonic oxide, carbonic anhydride, and hydrogen—together with other bodies, which are liquid or solid at common temperatures, whilst a considerable portion of charcoal remains in the retort. Of the liquid products, one portion is soluble in water, and consists of acetic acid, methylic alcohol, methylic acetate, and acetone, accompanied by water and other bodies but imperfectly known; while the remaining portion is insoluble in water, and constitutes wood-tar, which is a mixture of various liquids holding solid matters in solution or suspension. (See TAR, p. 670.)

The products of the distillation of wood, obtained at the lowest temperature, are those into the composition of which oxygen enters most abundantly—such as water, acetic acid, and carbonic acid. As the temperature rises, compounds containing less oxygen are gradually formed—such as wood-spirit, acetone, and creosote; at a still higher temperature, various hydrocarbons, such as toluene, xylene, eupione, and the different forms of paraffin, are produced; and as the temperature approaches redness, pure hydrogen predominates.

When air-dried hard woods, such as oak and beech, are distilled in iron cylinders, the charcoal amounts to about 25 per cent. of the weight of the wood, or about three-fifths of the quantity of carbon actually contained in it. The liquid portion, amounting to about 53 per cent., contains about one-fifth of the entire carbon in the wood; and the remaining portion of the distillate, consisting of uncondensed gas, carries off the remainder of the carbon. Among the liquid products, acetic acid amounts to between 3 and 4 per cent. of the harder woods, naphtha to about 1 per cent., and the tar to 7·5 per cent. (Miller's *Elements of Chemistry*, 3rd ed., iii. 702; for further details see Gmelin's *Handbook*, xv. 148–160.)

WOOD-OIL. *Capivi-balsam, Gurjun-balsam, Gwegun-balsam.* (Hanbury, Pharm. J. Trans. January, 1856, p. 321.—Martius, Buchn. N. Repert. v. 100.—Guibourt, *ibid.* vi. 97.—Werner, Zeitschr. f. Chem. 1862, p. 588.—A balsamic substance, much resembling balsam of copaiba (i. 492), imported of late years from Calcutta into this country for medicinal uses. It is obtained from several species of

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* Miller's *Elements of Chemistry*, 3rd. ed. iii. 149.

Dipterocarpus, growing in Pegu, Assam, and some of t
pelago. It smells and tastes like copaiba-balsam, is so
oil, and has a specific gravity of 0·964. In its original
presence of a greenish resin; when filtered from this, i
transmitted light, but opaque, with greenish fluoresce
colour and fluorescence distinguish it from copaiba-bals
observed in its behaviour when heated, and with reage
becomes turbid and gelatinous; whereas copaiba-balsam
temperature is raised. Wood-oil is less soluble in *alc*
viscid liquid with *ammonia*, whereas copaiba-balsam fo
over, wood-oil does not solidify when mixed with $\frac{1}{16}$ of i

Wood-oil is not a definite compound, but a mixture
cording to Lowe, it contains 34 per cent. resin, 65 v
acetic acid. The resin is hard, whereas that of copaiba

Werner, by distilling the balsam with water, obta
volatile oil, $C^{20}H^{32}$, polymeric with oil of turpentine.
of 9·014 at 15°, a lævorotatory power of 10°, boils
9·40 (2 vols.).

The resin left after distilling off the oil, contains a
$C^{22}H^{34}O^4$, soluble in aqueous ammonia. To separate
boiled with potash-ley, which dissolves it; the solutio
ammoniac, and filtered; and the ammoniacal filtrate is
which throws down the gurjunic acid in thick yellowi
in alcohol and ether, melts at 220°, solidifies at 180°
parently without decomposition. It is dibasic, and forn
and alkaline earths.—The *potassium-salt*, $C^{22}H^{32}K^2O$
microscopic laminæ.—The *calcium-salt*, $C^{22}H^{32}Ca''O^4$, an
are white and amorphous.—The *silver-salt*, $C^{22}H^{32}Ag^2O$
in white flocks, which blacken on exposure to light. (W

Wood-oil is used by the Malays as a varnish for ho
has been recommended as a substitute for copaiba-bals

WOOD-SPIRIT. See Methyl, Hydrate of (iii.

WOOD-TAR. See Tar (p. 670).

WOOL. (Schlossberger, Allgem. u. vergl. T
Besanez, Physiol. Chemie, p. 592.—Bolley, Hand
4te Aufl., p. 428.—Chevreul, J. pr. Chem. xxvii. 57:
Chemie, ii. 570.—Scherer, Ann. Ch. Pharm. xl. 54
Gorup-Besanez, *ibid.* lxvi. 321; cxviii. 230.—Grot
Lassaigne, J. Chim. Méd. xix. 562.)—Wool belongs
After exhaustion with water, alcohol, and ether, to re
contains, according to Scherer, 50·65 per cent. carbon,
and 24·61 oxygen and sulphur. Chevreul found in w
sulphur; Mulder rather more; v. Bibra 0·8–0·9 per
mean of numerous determinations with different kind
minimum being 1·3, and the maximum 3·4 per cent.

The amount of water in wool, is, according to M
per cent., of which 6 or 7 per cent. go off when the wo
air dry wool quickly takes up a considerable quantity
per hour according to Grothe's experiments.

In 100 pts. wool dried at 110°, Gorup-Besanez found
0·29 pt. silica, or 8·3 pts. silica in 100 pts. of ash. Res
sium-salts from the sweat of sheep's-wool, see Potassi

The reactions of wool with acids, alkalis, &c., are th
in general. Dilute alkaline solutions, especially soda-l
but the remainder appears to be more intimately com
by boiling with strong alkalis, which destroy the
Williams (Ann. Ch. Pharm. cix. 127), by distillin
potash-ley, obtained a distillate containing a large quan
butylamine and amylamine. Flannel distilled by itself
oil, accompanied by large quantities of pyrrol, stream
small quantity of carbonic disulphide, with mere traces

Wool and silk may be distinguished from vegetab
linen, by drawing out a thread and setting it on fire.
a shining, tumefied, difficultly combustible cinder, whic
when completely burnt; the smoke smells like burnt h

Vegetable fibres, on the other hand, leave a cinder having the form of the thread, and only a small quantity of ash; they burn with a smoke which has an empyreumatic odour, and reddens litmus. Wool and silk are also distinguished from cotton and linen by the yellow colour which they assume when steeped in *nitric* or in *picric acid*, the vegetable fibres not being coloured by this treatment. Wool or silk is dissolved by boiling with *potash-* or *soda-ley*, of specific gravity 1·04 to 1·05, whereas vegetable fibres remain unattacked. Cotton and linen dissolve in a solution of *cuprate of ammonium*, whereas wool is insoluble therein.

Wool and silk may be distinguished from one another by a solution of *sodic plumbate* (prepared by adding caustic soda to acetate of lead till the resulting precipitate redissolves), wool and hair being turned brown by this liquid, in consequence of the sulphur which they contain, whereas silk, which is free from sulphur, remains unaltered. The three following distinctions are given by Grothe (Zeitschr. anal. Chem. iii. 153): —1. Wool, cautiously heated to 130°, gives off the odour of carbonic disulphide and ammonia, assumes a golden-yellow colour, and curls up; silk becomes coloured only at 140°–145°, and does not curl up.—2. When the fibres, moistened with potash-ley, are dipped in a solution of *cupric sulphate*, and then exposed to the air, the wool quickly turns brown, in consequence of the formation of cupric sulphide, whereas the silk remains unchanged.—3. On mixing the solution of wool in caustic potash with *tartaric acid*, and then with *cupric sulphate*, a large quantity of cupric sulphide is formed, and the filtered liquid exhibits a dark brown-red colour. Silk treated in the same manner, yields a somewhat viscid solution having a fine violet colour.

WOORARA. Syn. with CURARA (ii. 185).

WOOTZ. *East Indian*, or *Persian Damask Steel.*—A very hard steel, made in India, and containing small quantities of silicon, manganese, nickel, and tungsten. It has a specific gravity of 7·727 at 17°, and exhibits very beautiful patterns when etched with acids.

WORMSEED. *Semen Cinæ. Semen Contra. Semen Santonici.*—The flower-buds of *Artemisia Vahliana, A. Sieberi*, and *A. inculta*, plants belonging to the composite order. The first is indigenous in Persia and Asia Minor, and yields Levant wormseed; the second grows in Barbary, Persia, and Arabia, and yields the Barbary or African wormseed; the third is said to yield the East Indian wormseed, which however, according to some authorities, is merely the African variety mixed with turmeric or fustic.

Wormseed contains santonin (p. 189), a volatile oil, a brown bitter resin, a green soft resin, and a waxy substance, together with the ordinary plant-constituents. It is used, especially the Levant variety, as a remedy for ascarides, being given either as an electuary or an infusion. It is not known which of the constituents of wormseed is the active principle.

WORMSEED-OIL. *Oleum cinæ. Essence de Semen-contra.* (Trommsdorff, Tr. N. J. iii. 312.—Völckel, Ann. Ch. Pharm. xxxviii. 110; lxxxvii. 312; Jahresb. 1853, p. 512; 1854, p. 590.—Hirzel, Jahresb. 1854, p. 591; 1855, p. 655.—Kraut and Wahlforss (Ann. Ch. Pharm. cxxviii. 293; Jahresb. 1863, p. 551.—Gm., xiv. 316.)—This oil is obtained by distilling wormseed with water. It has a pale-yellow to brownish-yellow colour, a pungent disagreeable odour, and camphorous, aromatic, burning taste; specific gravity = 0·925 to 0·935 (Wackenroder; Zeller; Völckel); 0·94 (Hirzel). It boils at 170°—180° (Hirzel). When distilled with milk of lime, it yields a lighter oil, of specific gravity 0·945° at 8°, and boiling between 174° and at 177°.

Wormseed-oil is a mixture of several oils, the proportions of which seem to vary considerably in different samples: hence the investigations of different chemists respecting it have yielded very discordant results. According to Kraut and Wahlforss, the oil, when purified by rectification with alcoholic potash, consists mainly of an oxygenated oil, $C^{10}H^{18}O$, having a lævorotatory power of 2·1°, mixed with a camphene, $C^{10}H^{16}$ (Völckel's cynene).

Wormseed-oil dissolves in about 1000 pts. of water, easily in ether, in all proportions of absolute alcohol, and in an equal quantity of alcohol of specific gravity 1·85 (Zeller). In contact with the air, it thickens and becomes coloured; it is easily inflammable.—With dilute *nitric acid*, it yields oxalic acid (Völckel), or toluic acid (Hirzel); when heated with strong nitric acid, it is converted into a yellow resin.

Iodine dissolves in wormseed-oil without evolution of heat. By dissolving 1 pt. of iodine in 4 to 6 pts. of the oil, with aid of heat, a dark brown-red, opaque, viscid mass is obtained, from which, on cooling, black crystalline laminæ separate (consisting of iodine and cinæbene?). From the solution of iodine in wormseed-oil, water extracts acetic, propionic, and hydriodic acids, and perhaps also iodide of propyl. On distilling the solution of iodine in wormseed-oil, propionic acid and iodoform pass over, together with a dark-brown mobile oil, containing cinæbene, hydriodate of cinæbene, cinæbene-camphor, cymene, and small quantities of cinacrol, angelic acid, &c., while the solid blue-black residue consists chiefly of cinæphene, cinæphane, and cinæphone (Hirzel). Wormseed-oil, mixed with a saturated solution of iodine in potassium-iodide, yields greenish metallic-shining crystals of the compound $2(C^{10}H^{18}O.H^{2}O).I^{2}$, which, when treated with alcoholic potash, reproduces wormseed-oil. (Kraut and Wahlforss.)

Sulphuric acid colours wormseed-oil red-brown, and on applying heat, sulphurous anhydride is evolved.—*Phosphoric anhydride* blackens it, and, according to Völckel, forms cynene; according to Hirzel, cinæbene, cinæphene, and cinacrol.—*Hydrochloric acid gas* is absorbed by wormseed-oil, forming a red-brown liquid, which on standing, deposits **wormseed-camphor**, in colourless slender needles having an aromatic camphor-like odour and mild warm taste; they deliquesce in the air, melt when heated, and yield, by distillation, an oil containing hydrochloric acid. (Hirzel and Völckel.)

Wormseed-oil distilled with *potassium-hydrate* yields a colourless, transparent, mobile oil, having a peppery odour and warm taste, a specific gravity of 0·932, and boiling at about 175°. With hydrochloric acid gas, this oil forms shining deliquescent needles; with nitric acid, liquid and resinous products; sulphuric acid colours it dark-brown, and renders it viscid. This oil has a composition represented by the empirical formula $C^{24}H^{40}O^{2}$, and consists, according to Hirzel, of cinæbene, cinæbene-camphor, propione, and a body containing $C^{10}H^{16}O$.

Derivatives of Wormseed-oil.

Cinæbene, $C^{10}H^{16}$ (with which Völckel's cynene is probably identical), exists ready-formed in wormseed-oil, and is separated by distilling the oil with phosphoric anhydride (Hirzel). It is a colourless, mobile, pungent, strongly-refracting oil, having a density of 0·878 at 16°, and boiling at 172°. When distilled with an equal volume of nitric acid of specific gravity 1·16, it yields acetic acid, propionic acid, and volatile oil, and leaves a resin, which, by prolonged boiling with excess of nitric acid, is converted into toluic and nitrotoluic acids, together with an oil, probably anisylous acid; no oxalic acid is formed in this reaction.—With *hydriodic acid*, cinæbene forms an oily hydriodate, $2C^{10}H^{16}.HI$.

Cinæbene-camphor, $C^{10}H^{18}O$, is contained, according to Hirzel, in wormseed-oil, but cannot be separated from it in the pure state. With phosphoric anhydride it is resolved into water and cinæbene. According to Kraut and Wahlforss, wormseed-oil, purified by alcoholic potash, consists of an oil, $C^{10}H^{18}O$, mixed with the camphene, $C^{10}H^{16}$, which cannot be separated by fractional distillation.

Cinæphene, $C^{20}H^{32}$, is one of the compounds formed by the action of phosphoric anhydride or iodine on wormseed-oil. It is an oil, viscid at ordinary temperatures, mobile when warm, boiling at 315°—325°, colourless by transmitted light, and exhibiting a deep indigo-blue iridescence by reflected light. When heated with nitric acid, it is converted into a resin having a musk-like odour. (Hirzel.)

Cinæphane, $C^{10}H^{8}$, is a resinous hydrocarbon found in the residue left on distilling wormseed-oil with iodine. To separate it, this residue is boiled with alcohol, which dissolves cinæphene; the remaining portion is dissolved in chloroform; the solution is mixed with 20 pts. of alcohol of specific gravity 0·84; and the resulting precipitate of cinæphane and cinæphone is treated with ether, which dissolves the latter, and leaves the cinæphane, to be further purified by solution in chloroform, precipitation with alcohol, and washing with ether. Cinæphane is a nearly velvet-black, loose, resinous powder, tasteless and inodorous; when heated it burns away without melting.

Cinæphone, $C^{10}H^{12}$, separated from cinæphene by ether in the manner just described, is a loosely coherent kermes-brown powder, destitute of taste and odour, insoluble in water and in alcohol, but soluble in ether, chloroform, and wormseed-oil; when heated, it burns and decomposes. (Hirzel.)

Cinacrol, $C^{10}H^{18}O^{2}$, is obtained by rectifying the oil produced by distilling 1 pt. of iodine with 4 to 6 pts. of wormseed-oil; agitating the nearly black liquid which passes over with strong potash-ley; heating the resulting dark-brown solution till it is nearly inodorous; and then distilling it with dilute sulphuric acid. The oil thus obtained is, after drying and rectification, colourless and viscid, with a faint smoky odour, and sharp caustic taste; a specific gravity of 1·05 to 1·15; boils at about 250°; dissolves slightly in water, easily in alcohol, ether, and acetic acid; still more easily in alkalis, forming a solution which gives a white precipitate with basic acetate of lead, a blue-green liquid with ferric chloride, and reduces nitrate of silver when heated with it. (Hirzel.)

WOULFE'S APPARATUS. An apparatus consisting of a series of three-necked bottles connected by suitable tubes, and used for washing gases or saturating liquids therewith.

WRIGHTINE. A basic substance obtained from the bark and seeds of *Wrightia antidysenterica* (*Nerium antidysentericum*, L.), an apocynaceous plant indigenous in India and Ceylon. To prepare it, the pulverised seeds are treated with carbonic disulphide in a displacement-apparatus, to remove a fat-oil, then dried and exhausted with hot alcohol; the extract, freed from alcohol by distillation, is digested with a small quantity of dilute hydrochloric acid; and the evaporated filtrate is mixed with ammonia or sodic carbonate, which throws down a copious flocculent precipitate consisting of the impure base.

Wrightine, after washing with cold water, forms an amorphous powder, insoluble in ether and in carbonic disulphide, soluble in water and alcohol, and especially in dilute acids, with which it forms uncrystallisable salts, having, like the base itself, a persistent bitter taste. The acetic acid solution is precipitated by tannic acid: the hydrochloric acid solution gives flocculent precipitates with platinic, auric, and mercuric chlorides. (Stenhouse, Pharm. J. Trans. [2], v. 493.)

R. Haines (*ibid.* vi. 432) states that he obtained the same base from the bark of *Wrightia dysenterica* (conessi-bark) in 1858, and gave a short description of it in the *Transactions of the Medical and Physical Society of Bombay* (new series, iv. 38). He proposes to call it conessine, and calculates, from the analysis of the free base and of the platinum-salt, the formulæ $C^{26}H^{42}N^2O$ and $C^{25}H^{44}N^2O$.

WULFENITE. Native molybdate of lead. (See Molybdenum, iii. 1039.)

WURTZITE. This name is given by Friedel (Compt. rend. lii. 983) to a hexagonal zinc-sulphide from the silver-mine of Oruro in Bolivia, containing 55·6 per cent. zinc, 32·6 sulphur, 8·0 iron, and 2·7 lead, with a little antimony and a trace of copper. It is isomorphous with greenockite, has a brownish-black colour, vitreous lustre, brown streak; hardness = 3·5, and specific gravity = 3·98.

X

XANTHAMIDE. Syn. with ethylic oxysulphocarbamate. (See Sulphocarbamic Ethers, p. 491.)

XANTHAMYLAMIDE. Amylic oxysulphocarbamate (p. 493).

XANTHAMYLIC ACID. Syn. with amyl-disulphocarbonic acid. (See Sulphocarbonic Ethers, p. 496.)

XANTHAMYLIC ETHER. Amylic disulphocarbonate (p. 496).

XANTHAN. Berzelius's name for the group Cy^2S^3, regarded as the radicle of persulphocyanic or xanthydric acid.

XANTHARIN, or **XANTHIL.** An oily fetid compound, $C^4H^{10}O^3$, supposed by Couerbe (Ann. Ch. Phys. [2], lxi. 225) to be produced by the dry distillation of xanthic ether.

XANTHAZARIN. A yellow colouring-matter, produced, according to E. Kopp (Jahresb. 1864, p. 815), by the action of nitric acid on the black residue obtained in preparing pure alizarin from his green alizarin (see Madder, iii. 749). It is slightly soluble in water, easily in alcohol, ether, and caustic alkalis. By heating with reducing agents, it is converted into a crimson substance.

XANTHEÏN. The name applied by Frémy and Cloez to that portion of the yellow colouring-matter of flowers which is soluble in water. (See Flowers, Colours of, ii. 668.)

XANTHELENE. Zeise gave this name to an oil (identical, according to Debus, with ethyl-disulphocarbonic sulphide, i. 499), produced, together with cuprous xanthate, by precipitating potassic ethylsulphocarbonate with a cupric salt. (Handw. d. Chem. 2te Aufl. i. 250.)

XANTHENE. Völckel, by heating persulphocyanic acid to about 150°, obtained a peculiar body, $C^3H^4N^4S^2$, which he regarded as a sulphide of xanthene, $C^3H^4N^4$; it was probably only a mixture.

XANTHIC ACID. Syn. with ethyl-disulphocarbonic acid. (See Sulphocarbonic Ethers, p. 498.)

XANTHIC ETHERS. Ethylic xanthate or disulphocarbonate (p. 500).

XANTHIC OXIDE. Syn. with XANTHINE.

XANTHIDES. Syn. with PERSULPHOCYANATES (iv. 379).

XANTHIL. Syn. with XANTHARIN.

XANTHIN. This name has been applied to more than one substance:—1. By Frémy and Cloez, to that portion of the yellow colouring-matter of flowers, which is insoluble in water (ii. 668);—2. By Schunck and Higgin, to the yellow colouring-matter obtained by Kuhlmann from madder (iii. 743);—3. By Couerbe, to a gaseous product of the decomposition of xanthates, to which he assigned the formula $C^2H^2S^2O^2$.

XANTHINE. $C^5H^4N^4O^2$. *Xanthic Oxide.* (Marcet, *Essay on the Chemical History and Chemical Treatment of Calculous Disorders*, London, 1819.—Liebig and Wöhler, Ann. Ch. Pharm. xxvi. 340.—Göbel, Jahresb. 1851, p. 604; 1852, p. 712.—Scherer, Ann. Ch. Pharm. cvii. 314; cxii. 257, 275, 279; Jahresb. 1858, p. 546; 1859, p. 605.—Strecker, Ann. Ch. Pharm. cviii. 141; cxviii. 151; Jahresb. 1858, p. 546; 1861, p. 526.—Städeler, Ann. Ch. Pharm. cxi. 28; cxv. 102; Jahresb. 1859, p. 603; 1860, p. 579.—Bence-Jones, Chem. Soc. Qu. J. xv. 78.—Almén, Jahresb. 1862, p. 534.—Strecker and Rheineck, Ann. Ch. Pharm. cxxxi. 121.)—This body was discovered by Marcet in a urinary calculus weighing only 8 grains. Liebig and Wöhler afterwards found it in a larger calculus weighing between 18 and 20 grammes; these are the only known examples of xanthine calculi. Bence-Jones found in it a deposit from the urine of a boy. According to Scherer, xanthine is a normal constituent of the human body; he has found it in the urine of man, in the pancreas, spleen, and liver of oxen, in the thymous gland of the calf, the muscular flesh of the ox, horse, and of fishes; also in the spleen, in a case of tumour of that organ; and in the human liver, in acute yellow atrophy. In the muscular flesh of the horse it exists to the amount of 0·0026 per cent., together with hypoxanthine or sarcine; in the pancreas to the amount of 0·0166 per cent., together with guanine; in the spleen, liver, and brain, together with uric acid. Almén found 0·02 per cent. xanthine in ox-liver. According to E. Dürr (Jahresb. 1865, p. 675), the presence of xanthine in human urine is promoted by the use of sulphur-baths. According to Unger and Phipson (Chem. News [1862], vi. 16), xanthine is found in certain kinds of guano from the island of Jarvis.

Artificial Formation.—Xanthine is produced:—1. From uric acid, from which it differs by 1 at. O, by the action of sodium-amalgam (Rheineck).—2. From guanine, from which it differs by NH, by the action of nitrous acid (Strecker):

$$2C^5H^5N^5O + O^2 = 2C^5H^4N^4O^2 + H^2O + N^2.$$

Preparation.—1. From *Urinary Calculi*, and from *Jarvis Guano*.—By dissolving the substance in aqueous potash or ammonia, and precipitating with carbonic or acetic acid.

2. From *Muscular Flesh* and other *Animal Substances*.—The substance, comminuted by trituration with pounded glass, is digested with warm alcohol and pressed; the residue is digested for some hours with water at 50°; the expressed liquid is mixed with the alcoholic solution, evaporated, and filtered to separate albumin; and the filtrate is successively precipitated with neutral lead-acetate, basic lead-acetate, and mercuric acetate. The two latter precipitates are then suspended in water, and decomposed by sulphydric acid; and the filtered liquid is evaporated, whereby a mixture of xanthine and sarcine is obtained, which may be separated by solution in hydrochloric acid—hydrochlorate of xanthine then separating out, while the greater part of the sarcine remains in solution. (Städeler.)

3. From *Guanine*.—The solution of guanine in strong nitric acid is mixed, at the boiling heat, with nitrite of potassium, till a copious evolution of red fumes takes place. A large quantity of water is then added; the yellow body thereby precipitated (a mixture of xanthine and nitroxanthine) is washed with water and dissolved in boiling carbonate of ammonia; and the solution is mixed with ferrous sulphate (to reduce the nitroxanthine to xanthine), till the red-brown precipitate of ferric hydrate at first produced is replaced by black ferroso-ferric oxide. The solution, which should still contain a large quantity of free ammonia, is then filtered, and evaporated to dryness over the water-bath; the residue is treated with cold water to extract sulphate of ammonium, then redissolved in boiling carbonate of ammonium; and the filtrate is evaporated, whereupon xanthine remains.

4. From *Urine*.—The urine is precipitated with baryta-water; the filtrate is evaporated; the highly concentrated mother-liquor boiled, after addition of water, with cupric acetate; the precipitate, after washing with hot water, is dissolved in warm

nitric acid, and precipitated with nitrate of silver; the washed precipitate is crystallised from hot dilute nitric acid; the resulting crystals are treated with ammoniacal silver-solution, to free them from nitric acid; and the washed precipitate is suspended in water, and decomposed by sulphydric acid. The filtrate, when evaporated, yields xanthine.

Properties.—Xanthine separates on cooling, from a hot saturated solution, in white flocks; by spontaneous evaporation in small scales. It is nearly insoluble in cold water (requiring 14,000 pts.), and but sparingly soluble in boiling water. It is insoluble in alcohol and in ether. The aqueous solution quickly putrefies.

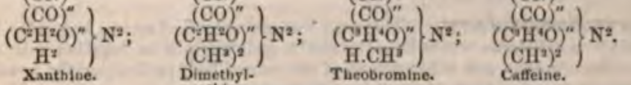
Xanthine does not lose weight at 150°; at a stronger heat, a small portion of it sublimes undecomposed, while the greater part decomposes, yielding carbonate and cyanide of ammonium, and a yellow oil, but no urea. When heated in contact with the air, it burns with the smell of burnt hair.—By the action of sodium-amalgam containing a very small proportion of sodium, xanthine is reduced to sarcine, $C^5H^4N^4O$, this base being in fact produced, together with xanthine, by the action of sodium-amalgam on uric acid (p. 1050).

Combinations.—Xanthine unites both with acids and with bases, forming for the most part crystallisable compounds, which are more soluble than xanthine itself.—The *hydrochlorate*, $C^5H^4N^4O^2.HCl$, forms nodular groups of small silky crystals. Its aqueous solution mixed with *platinic chloride* deposits yellow needles of a double salt.—The *nitrate* separates from a solution of xanthine in warm moderately strong nitric acid, in yellow warty masses. The solution of xanthine in nitric acid forms, with *phosphomolybdic acid*, a yellow precipitate, which dissolves in hot moderately strong nitric acid, and separates, on cooling, in yellow microscopic cubes (Scherer).—The *sulphate*, $C^5H^4N^4O^2.H^2SO^4 + H^2O$, forms thin, transparent, crystalline scales, which are decomposed by water.

A solution of xanthine in *ammonia*, saturated at the boiling heat, deposits, on cooling, crystals of xanthine-ammonia. On boiling xanthine with *baryta-water*, a sparingly soluble compound, $C^5H^4N^4O^2.Ba''H^2O^2$, is produced. (Strecker.)

A cold saturated aqueous solution of xanthine gives white precipitates with mercuric chloride and silver nitrate, yellowish-green flocks with cupric acetate. The ammoniacal solution of xanthine gives white precipitates with the chlorides of mercury, zinc, and cadmium; with nitrate of silver, it forms yellowish-white flocks of the compound $C^5H^4N^4O^2.Ag^2O$, which turn black on boiling.—From a solution of xanthine in nitric acid, silver-nitrate throws down flocks, probably consisting of a compound of xanthine with silver-nitrate, which, if left in the hot liquid, gradually become crystalline; water abstracts nitric acid from them.

The silver-compound of xanthine, heated with methylic iodide, yields **dimethylxanthine**, $C^5H^2(CH^3)^2N^4O^2$, isomeric but not identical with theobromine. Strecker represents the relation between these three bases and caffeine by the following rational formulæ:



$$\left.\begin{array}{c}(CN)^2\\(CO)''\\(C^2H^2O)''\\H^2\end{array}\right\}N^2;\quad \left.\begin{array}{c}(CN)^2\\(CO)''\\(C^2H^2O)''\\(CH^3)^2\end{array}\right\}N^2;\quad \left.\begin{array}{c}(CN)^2\\(CO)''\\(C^3H^4O)''\\H.CH^3\end{array}\right\}N^2;\quad \left.\begin{array}{c}(CN)^2\\(CO)''\\(C^3H^4O)''\\(CH^3)^2\end{array}\right\}N^2.$$

Xanthine. Dimethyl-xanthine. Theobromine. Caffeine.

XANTHININE. $C^4H^3N^3O^2$. (C. Finck, Ann. Ch. Pharm. cxxxii. 298; Jahresb. 1864, p. 642.)—A base produced, together with sulphate of ammonium, by heating thionurate of ammonium to 200°:

$$C^4H^3(NH^4)^2N^3SO^6 \;=\; (NH^4)^2SO^4 \;+\; C^4H^3N^3O^2.$$

On boiling the resulting mass with water, the xanthinine remains as a yellow powder, which may be purified by solution in alkalis, precipitation with acids, and treatment with strong nitric acid. It dissolves in about 4,000 pts. of boiling and 40,000 pts. of cold water, to a light-blue fluorescent solution, which is precipitated white by mercuric chloride, yellow by silver-nitrate. It dissolves in strong nitric and hydrochloric acids, somewhat more freely than in water, and separates therefrom in crystalline laminæ. The solution in concentrated sulphuric acid, decolorised with a little nitric acid, deposits sulphate of xanthinine in laminar crystals, which are decomposed by water, with separation of white pulverulent xanthinine. On dropping an ammoniacal solution of xanthinine into an excess of silver-nitrate, a bulky yellow silver-compound, $C^4H^3N^3O^2.Ag^2O$, is formed, insoluble in water and in ammonia.

XANTHINOCARPIN. A yellow colouring-matter, contained, according to Cuzent (Jahresb. 1859, p. 564), in the juice which exudes from incisions in the bark or fruit of *Inocarpus edulis*.

XANTHIN-SPAR. Syn. with Wulfenite (p. 1049).

XANTHITANE. A mineral from Green River, in Henderson County, North Carolina, probably a pseudomorph after titanite. It is earthy, yellowish-white, with faint lustre; brittle; hardness = 3·5; specific gravity = 2·7 to 3·0. Gives off water when heated in a tube, and exhibits with fluxes the reactions of titanium. (Shepard, J. pr. Chem. Bd. lxix.)

XANTHITE. A variety of vesuvian occuring at Amity, in the State of New York, in indistinct, four-sided, prismatic crystals and crystalline granules, imbedded in limestone. (Dana, ii. 199.)

XANTHOBETIC ACID. An acid contained, according to L. Meier, in the root of *Beta vulgaris*. It is obtained by precipitating the cold aqueous extract with neutral acetate of lead, boiling the precipitate repeatedly with water, then drenching it with alcohol of 80 per cent., and evaporating the extract to dryness after addition of dilute sulphuric acid. On exhausting the brown residue with cold alcohol, and evaporating, xanthobetic acid remains as a reddish-yellow mass, having a sour taste, very hygroscopic, slightly soluble in ether, easily in alcohol and in water. Alkalis and alkaline earths colour it red, and form soluble crystalline salts, from which the xanthobetic acid is separated by stronger acids in its original state. The xanthobetates of the heavy metals are insoluble, and are obtained by precipitation. (Handw. d. Chem. ix. 828.)

XANTHOCHYMUS. The juice of *Xanthochymus pictorius* (formerly supposed to contain gamboge) is greyish-green, and contains 65·5 per cent. resin, 17·6 gum, and 5·9 woody fibre; no volatile oil. (Christison, Ann. Ch. Pharm. lxxvi. 347.)

XANTHOCOBALTIC SALTS. See Cobalt-bases, Ammoniacal (i. 1054); for the view of their composition proposed by C. D. Braun, see Jahresb. 1862, p. 210; 1864, p. 270.

XANTHOCONE. $Ag^3AsS^4.2Ag^3AsS^3$.—A silver-ore from the Himmelfürst mine, near Freiberg in Saxony, crystallising, according to A. Breithaupt (Pogg. Ann. lxiv. 272), in rhombohedral plates, having a brown to orange-yellow colour and adamantine lustre; transparent to translucent, somewhat brittle; hardness = 2·3; specific gravity = 5·0 to 5·2.

XANTHOCYSTIN. See Tyrosine (p. 931).

XANTHOGEN. A name applied by Hope (J. pr. Chem. x. 269) to a substance (called "resin of flowers" by Clamor-Marquart), which he supposed to be very widely diffused in the vegetable kingdom, and to be turned yellow by alkalis. (See Flowers, Colours of, ii. 668.)

XANTHOGEN-OIL. Zeise's name for an oily product formed by the dry distillation of potassic xanthate (p. 498).

XANTHOGLOBULIN. This name was given by Scherer (Ann. Ch. Pharm. cxii. 257) to a substance which he obtained in yellow globules, together with sarcine, from the liver, spleen, and other organs of the animal body; subsequently, however, he found that it was a mixture of xanthine and sarcine.

XANTHOLCIN. A yellow colouring-matter from the seed-capsules of *Sorghum saccharatum*.

XANTHOLEIN. A yellow colouring-matter obtained from the bark of *Sorghum saccharatum*. (Secard, Itier, and Joulie, Compt. rend. xliv. 19, 141.)

XANTHOMETHYLIC ACID. See Sulphocarbonic Ethers (p. 501).

XANTHOPENIC ACID. A product of the decomposition of opiammone by aqueous alkalis (iv. 207).

XANTHOPHENIC ACID. A yellow colouring-matter, of unknown composition, produced, according to Fol (Rép. Chim. App. 1862, p. 179; Jahresb. 1862, p. 697), by heating phenol or cresol with arsenic acid. It dissolves in water with golden-yellow colour, in aqueous alkalis with red colour, and forms reddish salts. The free acid dyes silk and wool yellow, without the aid of mordants, and the dyed stuffs may be treated with soap. The xanthophenates dye silk and wool red, of various shades, from the darkest red to the lightest rose-colour.

XANTHOPHYLL. The yellow colouring-matter of withered leaves. Nothing certain is known respecting its composition, or of the manner in which it is formed from chlorophyll. (See Handw. d. Chem. 2^{te} Aufl. ii. [2], 10, art. Blattgrün.)

XANTHOPHYLLITE. See CLINTONITE (i. 1026).

XANTHOPICRIN. XANTHOPICRITE. These names were given, by Chevallier and Pelletan (Ann. Ch. Phys. [2], xxxiv. 200), to a yellow colouring-matter from the bark of *Xanthoxylon caribæum*, since shown by Perrins (Pharm. J. Trans. [2], iv. 465), to be identical with berberine (i. 579).

XANTHOPROTEIC ACID. An acid formed by the action of nitric acid on albumin, fibrin, casein, and horny matters. It is purified by boiling water and alcohol (Mülder, J. pr. Chem. xvi. 397; xx. 352). It is an orange-yellow, amorphous, inodorous, and tasteless substance, which reddens vegetable colours. It is charred by heat without melting, diffusing an odour of burnt horn; forms deep red solutions with alkalis, and is precipitated therefrom by acids. Dissolves in concentrated acids, and is precipitated by water from the acid solutions in combination with the acid employed. These precipitates are decomposed by washing:—

	Mülder.	Van der Pant. (Average of 11 analyses.)
Carbon . . .	50·78	50·0
Hydrogen . . .	6·60	6·3
Nitrogen . . .	14·00	14·7
Sulphur . . .	"	1·3
Oxygen . . .	"	"

Mülder considers xanthoproteic acid to be dibasic, and ascribes to it the formula $C^{34}H^{26}N^{4}O^{14}$. Xanthoproteic acid is decomposed by boiling concentrated *potash*, yielding ammonia. When *chlorine* is passed through an ammoniacal solution of the acid, the liquid is decolorised, and a yellow precipitate, containing chlorine, is formed.

The *potassium-* and *sodium-salts* do not crystallise; they have a fine red colour.—The *ammonium-salt* is red, and parts with all its ammonia at 140°.—The *barium-* and *calcium-salts* are red, very soluble in water, and insoluble in alcohol and in ether.—The *barium-salt* contains 12·9 per cent. BaO (Van der Pant).—The *iron-* and *copper-salts* are orange, and become red on drying.—The *lead-salt* forms a yellow precipitate becoming red by desiccation, and contains 14 per cent. PbO.—The *silver-salt* resembles the preceding.

Neither the acid nor its salts explode by heat.

XANTHOPYRITE. Syn. with IRON PYRITES (iii. 403).

XANTHORHAMNIN. A yellow colouring-matter obtained from Persian or Turkey berries, the seeds of *Rhamnus amygdalinus*, *R. oleoïdes*, *R. saxatilis*, and from Avignon grains, the seeds of *R. infectorius* (p. 100). According to Kane (Phil. Mag. [3], xxiii. 3), it has the composition $C^{23}H^{24}O^{14}$, and occurs only in the ripe seeds, being formed by decomposition of the chrysorhamnin contained in the unripe seeds (i. 960). It is also produced by boiling chrysorhamnin with water, in contact with the air; and when unripe Persian berries are boiled with water for some time, and dried, they are afterwards found to contain, not chrysorhamnin, but xanthorhamnin. Xanthorhamnin dried in a vacuum over oil of vitriol, is deliquescent, melts below 100°, and continues to give off water till heated to 200°, and then solidifies to a brittle mass. It decomposes above 200°, dissolves easily in water and in alcohol, but is quite insoluble in ether. The aqueous solution is precipitated by neutral and basic acetate of lead. (Kane.)

According to Gellatly (N. Edinb. Phil. J. vii. 252), xanthorhamnin has the composition $C^{23}H^{28}O^{14}$, and exists ready-formed in the unripe berries. To obtain it, the coarsely-ground berries are boiled with alcohol; the tincture, not too concentrated, is freed by standing and repeated decantation from a dark-brown resin, and then left for some days to crystallise; and the product is purified by crystallisation from alcohol. Xanthorhamnin thus obtained forms compact tufts of pale-yellow shining crystals containing 5 at. water, which they give off without melting at 100°. In aqueous solution it is resinised by bromine and chlorine. Nitric acid oxidises it, forming a red solution which contains oxalic acid. It dissolves in strong sulphuric acid, and is thrown down as a yellow precipitate by water. By boiling with dilute acids, it is resolved into rhamnetin and glucose:

$$\underset{\text{Xanthorhamnin.}}{C^{23}H^{28}O^{14}} + 3H^{2}O = \underset{\text{Rhamnetin.}}{C^{11}H^{10}O^{5}} + \underset{\text{Glucose.}}{2C^{6}H^{12}O^{6}}.$$

Xanthorhamnin dissolves easily in water, either hot or cold, but cannot be separated from the solution in the crystalline form. It dissolves in cold alcohol, easily in boiling alcohol, but is insoluble in ether. With aqueous alkalis it forms brown solutions, which become paler when mixed with acids. It forms precipitates with salts of the alkaline earth-metals, aluminium-salts, and stannic salts. Neutral lead-acetate, mixed with an excess of alcoholic xanthorhamnin, gives a yellow precipitate, consisting, in the air-dried state, of $C^{23}H^{28}O^{14}.PbO$. Xanthorhamnin forms a black precipitate with iron-salts. It dyes fabrics mordanted with alumina, a fine yellow; those mordanted with iron, black. (Gellatly.)

Hlasiwetz (Ann. Ch. Pharm. cxi. 108) regards xanthorhamnin as identical with quercitrin (p. 6) and rhamnetin resulting from its decomposition as identical with quercetin (p. 4). This is doubted by Bolley (*ibid.* cxv. 55), who, however, obtained quercetin from Persian berries (Chem. Soc. Qu. J. xiii. 328); also by Gellatly (Chem. News, iii. 196; Jahresb. 1860, p. 497).

XANTHORRHŒA RESIN. Syn. with ACAROÏD RESIN (i. 2).

XANTHORTHITE. A yellow mineral from the Kullberg, near Stockholm, allied to orthite or allanite, and containing, according to Bahr (Berz. Jahresb. xxvi. 369), 32·93 per cent. SiO^2, 15·54 Al^2O^3, 4·21 FeO, 20·01 CeO (with LaO and DiO), 6·76 CaO, 0·59 YO, 2·15 MgO, 0·39 MnO, 17·55 water, and a small quantity of carbonic acid.

XANTHOSIDERITE. A hydrated ferric oxide, $Fe^2O^3.2H^2O$, occurring in acicular or fibrous crystalline groups, near Ilmenau in the Thuringian Forest. (E. Schmid, Pogg. Ann. lxxxiv. 495.)

XANTHOTANNIC ACID. The name given by Ferrein (Jahresb. 1858, p. 463) to the yellow colouring-matter of elm-leaves, which he regards as a tannic acid. The alcoholic extract of yellow elm-leaves gave, when treated with water, a yellow-brown liquid, from which acetate of lead threw down xanthotannate of lead, $3PbO.2C^{14}H^{18}O^2$.

XANTHOXYLENE. $C^{10}H^{16}$. (Stenhouse, Pharm. J. Trans. xvii. 19.)—The volatile oil of *Xanthoxylon piperitum*, Dec. (*Fagara piperita*, L.), the so-called Japan-pepper. It is colourless, strongly refractive, has an aromatic odour not altered by treatment with sodium; boils at 162°; forms a liquid compound with hydrochloric acid.

XANTHOXYLIN. (Stenhouse, Pharm. J. Trans. xiii. 423; xvii. 19.)—A crystalline non-nitrogenous camphor or stearoptene, which separates, on cooling, from the oil obtained by distilling the bruised seeds of *Xanthoxylon piperitum* with water. It may also be prepared by evaporating the alcoholic extract of the fruit; the crystals thus obtained are contaminated with resin, but may be purified by washing with cold aqueous ammonia, and recrystallising from alcohol or ether-alcohol.

Xanthoxylin forms monoclinic crystals, having a silky lustre, a faint odour, and a slight aromatic taste. It is insoluble in water, but dissolves easily in alcohol and ether, melts at 80°, solidifies at 78°, and may be distilled without decomposition. Nitric acid oxidises it to oxalic acid. The alcoholic solution is not precipitated by nitrate of silver, or acetate of lead, even on addition of ammonia.

XANTHOXYLON. The bark of *X. caribæum*, Lum., or *X. Clava Herculis*, L., used in the Antilles as a febrifuge, contains, according to Staples (Pharm. J. Trans. [2], iv. 399), a volatile oil, a green fixed oil, gum, and a crystallisable bitter principle, designated by him as xanthoxylin, and regarded by Bentley (*ibid.*), as probably identical with the xanthopicrite of Chevallier and Pelletan (p. 1053); according to Perrins, however, the two bodies are distinct, xanthopicrite being in fact identical with berberine.

The fruit of *X. piperitum* contains a volatile oil, xanthoxylene, and a crystalline camphor, xanthoxylin (*vid. sup.*)

XANTHURIN. The name given by Couerbe to a liquid compound, $C^4H^8SO^2$, which he supposed to be produced by the dry distillation of potassic or plumbic xanthate.

XANTHYDRIC ACID. Syn. with PERSULPHOCYANIC ACID (iv. 378).

XENOLITE. An aluminic silicate, occurring at Peterhof in Finland, in fibrous layers having a vitreous lustre, hardness = 7·0, and specific gravity = 3·5. Contains 47·44 per cent. silica, and 52·54 alumina. (Komonen, Pogg. Ann. lvi. 643.)

XENOTIME. Native phosphate of yttrium. (See PHOSPHATES, iv. 586.)

XENYLAMINE. $C^{12}H^{11}N = \left.\begin{matrix}C^{12}H^9\\H^2\end{matrix}\right\}N$. *Martylamine.* (Hofmann, Proc. Roy. Soc. xii. 389.)—A monamine isomeric with diphenylamine, occurring in the basic oil, boiling above 130°, which is obtained as a bye-product in the manufacture of aniline. This mixture of oily bases, neutralised with sulphuric acid, deposits impure sulphate of xenylamine, which may be purified by treating it with boiling alcohol, crystallising the remaining salt from a large quantity of boiling water, and again treating it with boiling alcohol. On suspending the pure sulphate thus obtained in weak alcohol, decomposing it with caustic soda, and adding water, xenylamine separates in the crystalline form, and may be purified by solution in alcohol, and precipitation with water.

Pure xenylamine forms white shining scales or needles, having a slight grey tint when dry. It is but slightly soluble in boiling water, easily in alcohol and in ether; melts at 45°, boils at 320°, and distils without decomposition. It unites with acids, forming crystallisable salts.—The *hydrochlorate*, $C^{12}H^{11}N.HCl$, forms white needles, somewhat more soluble than the sulphate.—The *chloroplatinate*, $2(C^{12}H^{11}N.HCl).PtCl^4.H^2O$, is a pale-yellow precipitate, composed of microscopic needles; does not give off its water of crystallisation at 150°.—The *nitrate*, $C^{12}H^{11}N.HNO^3$, forms large white needles, moderately soluble in water.—The *sulphate*, $(C^{12}H^{11}N)^2.H^2SO^4$, is distinguished by its sparing solubility in cold and even in boiling water; it is but little more soluble in boiling alcohol. From the boiling aqueous solution it separates in small needles.

Derivatives of Xenylamine.

Xenylamine shows less tendency than most other monamines to the formation of substitution-derivatives.—With *bromine, chlorine*, and most oxidising agents, it yields black compounds, which crystallise with difficulty, or not at all.—When *nitrous acid gas* is passed into an alcoholic solution of xenylamine, the liquid soon solidifies to a red crystalline mass, consisting of an azodixenylamine, $C^{24}H^{19}N^3 = C^{24}(H^{19}\overset{'''}{N})N^2$, or a double molecule of xenylamine, in which 3 at. H are replaced by 1 at. $\overset{'''}{N}$:

$$4C^{12}H^{11}N + N^2O^3 = 2C^{24}H^{19}N^3 + 3H^2O.$$

This body is insoluble in water, slightly soluble in alcohol, freely in ether. When treated with acids, it yields xenylamine, and an aromatic substance not yet examined.

Diethyl-xenylamine, $C^{16}H^{19}N = \left.\begin{matrix}C^{12}H^9\\(C^2H^5)^2\end{matrix}\right\}N$, is obtained in aqueous solution by treating xenylamine with ethylic iodide and silver-oxide alternately. On evaporating the solution, it crystallises in long white needles, insoluble in water, moderately soluble in alcohol, easily in ether; it has no alkaline reaction, melts below 100°, and volatilises without decomposition at a higher temperature. It forms crystallisable salts with hydrochloric, hydrobromic, and hydriodic acids.

Diethyl-xenylamine is not further acted upon by iodide of ethyl.—With *iodide of methyl*, however, it yields an ammonium-base, which has an alkaline reaction in the free state, and forms a crystalline chloroplatinate, $2C^{17}H^{22}NCl.PtCl^4 = 2(C^{12}H^9)(C^2H^5)^2(CH^3)NCl.PtCl^4$.

XENYLENE-DIAMINE. This name is given by Hofmann to benzidine $\left.\begin{matrix}(C^{12}H^8)''\\H^4\end{matrix}\right\}N^2$ (i. 545; iv. 411), which is, in fact, related to xenylamine in the same manner as ethylene-diamine (ii. 585) is related to ethylamine.

XENYLENIC ALCOHOL. $C^{12}H^{10}O^2 = \left.\begin{matrix}(C^{12}H^8)''\\H^2\end{matrix}\right\}O^2$. *Diphenyl-alcohol. Diphenylic Acid.* (Griess, Chem. Soc. J. xx. 96.)—A diatomic alcohol, produced by the action of water on nitrate of diazobenzidine (iv. 412):

$$C^{12}H^8N^4.2HNO^3 + 2H^2O = C^{12}H^{10}O^2 + 2HNO^3 + 2N^2.$$

It crystallises in small white or slightly coloured plates or needles, slightly soluble in water, freely in alcohol or ether. It melts when heated, and may be sublimed by cautiously heating small quantities of it in a test-tube. It dissolves easily in potash, and is precipitated therefrom by acids. Strong aqueous ammonia also dissolves it, and the solution gives a white bulky precipitate with acetate of lead. Strong nitric acid converts it into a nitro-acid, which crystallises in yellow roundish crystals, and forms an ammonium-salt crystallising in long needles.

XERASITE. A decomposing lava-mass containing hornblende, from Vesuvius.

XILITE. Syn. with XYLITE.

XILOPOL. Syn. with XYLOPOL.

XUTHENE. The sulphide of this radicle, $C^8H^7H^9S^2$, was supposed by Völckel to be produced, together with several other doubtful compounds, by the decomposition of persulphocyanic acid (iv. 379).

XYLENE, or **XYLOL,** C^8H^{10} = *Dimethylbenzene*, $C^6H^4(CH^3)^2$; isomeric with

Ethylbenzene, $C^6H^5(C^2H^5)$.—This hydrocarbon, homologous with benzene and toluene, was first obtained in the pure state from coal-naphtha by Hugo Müller (Zeitschr. Ch. Pharm. 1864, p. 161), its trinitro-compound having been previously prepared from Burmese naphtha by Warren De la Rue, and Hugo Müller in 1856 (Proc. Roy. Soc. viii. 225). It was afterwards prepared in larger quantity from coal-naphtha, and further examined by Beilstein, Wahlforss, and Rössler (Ann. Ch. Pharm. cxxxiii. 32; Jahresb. 1864, p. 529).—Fittig, in 1864 (Ann. Ch. Pharm. cxxxiii. 47), showed that it may be formed synthetically, as dimethylbenzene (methylbenzyl).

Xylene had been obtained, mixed with toluene and other hydrocarbons, several years before it was completely isolated. The hydrocarbon (boiling at 128°—130°), obtained by Cahours (Compt. rend. xxx. 319), and by Völckel (Ann. Ch. Pharm. lxxxvi. 335), was evidently a mixture of xylene and toluene; so likewise was the so-called xylene (boiling at 126·2°), prepared by Church (Chem. Soc. J. xiv. 52) from coal-naphtha. Nearly pure xylene had previously been obtained from coal-naphtha by Mansfield, Ritthausen, and Hilkenkamp; but they regarded it as cumene. The hydrocarbon, boiling at 145°—148°, and likewise described as cumene, separated by Cahours (Ann. Ch. Pharm. lxxvi. 286) from crude wood-spirit, and the so-called retinyl, boiling at 150°, obtained by Pelletier and Walter (*ibid.* xxiii. 150; xxviii. 297), from the distillation-products of the resin of *Pinus maritima*, also consisted mainly of xylene. Lastly, the hydrocarbon called petrol (iv. 383), found by Bussenius and Eisenstück in the petroleum of Sehnde near Hanover, is evidently identical with xylene.

Preparation.—1. From Coal-naphtha.—Light coal-naphtha, or (better) the least volatile portion of that which has been distilled off in benzene manufactories (boiling at 130°—160°), is subjected to repeated fractional distillation, to separate the portion which boils at about 141°; this portion is shaken up with oil of vitriol containing a little fuming sulphuric acid, which dissolves the xylene as xylene-sulphuric acid, leaving undissolved a small quantity of a hydrocarbon of the marsh-gas series (probably $C^{10}H^{22}$, boiling at 151°), and of another having the composition of turpentine; the xylene-sulphuric acid is decomposed by dry distillation; and the xylene which passes over is purified by washing, drying, and distillation. (Beilstein.)

2. By synthesis.—By the action of methylic iodide and sodium on monobromotoluene (Fittig):

$$\underset{\text{Bromotoluene.}}{C^6H^4Br.CH^3} + CH^3I + Na^2 = NaBr + NaI + \underset{\text{Xylene.}}{C^6H^4(CH^3)^2}.$$

Properties and Reactions.—Xylene is a colourless liquid, having a very faint odour, different from that of benzene. Specific gravity = 0·86 at 19°. Boils constantly at 139°. According to Warren (Jahresb. 1865, p. 514), its specific gravity is 0·8780 at 0°, 0·866 at 15°; boiling-point (corrected) 139·8°. By oxidation with potassic bichromate and sulphuric acid, it yields terephthalic acid, $C^8H^6O^4$; dilute nitric acid converts it into the intermediate product, toluic acid, $C^8H^8O^2$:

$$C^8H^{10} + O^3 = C^8H^8O^2 + H^2O.$$
$$C^8H^{10} + O^6 = C^8H^6O^4 + 2H^2O.$$

Probably, in the former case, toluic acid is first formed, and then further oxidated to terephthalic acid; in fact, toluic acid is actually transformed into terephthalic acid by oxidation with chromic acid. (Beilstein and De Scheffer, Zeitschr. f. Chem. 1865, p. 212.)

Xylene, passed in the state of vapour through a red-hot tube, is resolved into a mixture of several hydrocarbons—viz., benzene; toluene; a hydrocarbon, C^8H^8, probably styrolene; naphthalene; liquid hydrocarbons boiling between 250° and 320°; anthracene, $C^{14}H^{10}$, and probably its higher homologues; and, lastly, orange-coloured hydrocarbons of resinous and bituminous consistence, analogous to chrysene, benzerythrene, &c. The formation of these products may be represented by the following equations:

$$\underset{\text{Xylene.}}{C^8H^{10}} - H^2 = \underset{\text{Styrolene.}}{C^8H^8}$$
$$\underset{\text{Xylene.}}{3C^8H^{10}} = \underset{\text{Toluene.}}{2C^7H^8} + \underset{\text{Naphthalene}}{C^{10}H^8} + 3H^2.$$

The anthracene, $C^{14}H^{10}$, is produced by the dehydration of toluene. (Berthelot, Bull. Soc. Chim. 1867, i. 227.)

Ethylbenzene, $C^6H^5.C^2H^5$.—This hydrocarbon, isomeric with xylene, is produced by the action of sodium on a mixture of monobromobenzene and ethylic bromide. It is a colourless mobile liquid, very much like toluene, and boiling constantly at 133°. By oxidation with potassic bichromate and sulphuric acid, it yields benzoic acid.

Derivatives of Xylene.

The chlorine- and bromine-derivatives of xylene have not been much investigated. Theoretically, they should exhibit isomeric modifications, similar to those of the toluene-derivatives (p. 852), but in greater number, inasmuch as xylene contains two atoms of methyl, whereas toluene contains only one. Thus there should be two xylylic chlorides corresponding to benzylchloride, the one being isomeric with monochloroxylene, the other with dichloroxylene; thus—

Monochloroxylene, $C^6H^2Cl\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.$, isomeric with $C^6H^4\left\{\begin{matrix}CH^3\\CH^2Cl\end{matrix}\right.$, first chloride.

Dichloroxylene, $C^6H^2Cl^2\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.$ „ „ $C^6H^4\left\{\begin{matrix}CH^2Cl\\CH^2Cl\end{matrix}\right.$, second chloride.

From experiments by Körner, it appears that both these chlorides are produced when xylene is treated with chlorine at the boiling heat.

Bromo-xylenes. (Riche and Bérard, Ann. Ch. Pharm. cxxxiii. 53.—Beilstein and Wahlforss, *ibid.* 46.—Fittig and Ernst, Zeitschr. Ch. Pharm. 1865, p. 572.) —When bromine is made to flow slowly into xylene, a large quantity of hydrobromic acid escapes, and the colour of the bromine disappears almost immediately. On shaking up the product with potash-ley, distilling over caustic potash (best with addition of a little alcohol, to prevent percussive ebullition), and purifying by fractional distillation, monobromoxylene, C^8H^9Br, is obtained as a colourless liquid, of specific gravity 1·335 at 20°, boiling at 212° (Wahlforss), at 203°—204° (Fittig and Ernst), at 203° (Kekulé). Its vapour does not excite tears.

The more highly brominated derivatives of xylene are produced in small quantity by the process just described (Kekulé). Riche and Bérard, by treating xylene with bromine for several days, obtained an oily product, which was converted by nitric acid into a crystallisable nitro-compound, $C^8H^6Br^3(NO^2)$; the bromine-compound was therefore tribromoxylene, $C^8H^7Br^3$.

Ethylbenzene is slowly attacked by bromine, forming monobromo-ethylbenzene, which is a liquid boiling at about 200°. When heated with bromine to 100°, it yields more highly brominated compounds, which are also liquid. (Fittig, Ann. Ch. Pharm. cxxxiii. 226.)

Chloro-xylenes. (Hollemann, Zeitschr. f. Chem. 1865, p. 554; Jahresb. 1865, p. 554.—Vollrath, Zeitschr. f. Chem. 1866, p. 488; Jahresb. 1866, p. 605.—Lauth and Grimaux, Bull. Soc. Chim. 1867, i. 233; Ann. Ch. Pharm. cxlv. 115.)

Monochloro-xylene, $C^6H^3Cl(CH^3)^2$, has not yet been obtained; but the isomeric compound, toluylic chloride, or chloride of toluyl, $C^6H^4\left\{\begin{matrix}CH^3\\CH^2Cl\end{matrix}\right.$, is produced by the action of chlorine on xylene at the boiling heat (Vollrath, p. 870), or by passing chlorine-gas into vapour of xylene, and subjecting the product to repeated fractional distillation (Lauth and Grimaux). It is a clear colourless liquid, which excites a copious flow of tears; boils between 190° and 195° (Lauth and Grimaux); at 193° (Vollrath). It precipitates a solution of *silver-nitrate* even in the cold, and when boiled with acetate of silver, yields chloride of silver and acetate of toluyl (p. 869). Heated for an hour with ½ mol. *nitrate of lead* and 6 or 7 times its weight of water, it is converted into toluic aldehyde, C^8H^8O (Lauth and Grimaux). It is decomposed by *sodium*, yielding toluyl, $(C^8H^9)^2$, and when treated with *cyanide of potassium*, in presence of alcohol, it yields alphaxylylic acid, $C^9H^{10}O^2$. (Vollrath.)

Dichloro-xylene, $C^8H^8Cl^2 = C^6H^2Cl^2\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.$, is produced by passing chlorine, nearly in the quantity required by theory, into xylene containing a small quantity of iodine, and purifying the product by fractional distillation. It crystallises in white laminæ, melts at the heat of the hand, and boils at 222°; dissolves easily in alcohol and in benzene. It does not exhibit double decomposition with acetate or cyanide of potassium, even at 120°.—*Sodium* attacks it readily, producing a solid hydrocarbon, not yet examined. (Hollemann.)

The same or an isomeric compound is produced, together with the monochlorinated compound, in the process just described, and is deposited in the solid form when the portions of the crude product which distil over between 230° and 240°, and between 240° and 250°, are cooled by a freezing mixture. It may be purified by pressure, and crystallises by slow evaporation from a large quantity of ether, or a mixture of ether and alcohol, in rather large, transparent, shining crystals. It melts at 100°, and solidifies to a radiate mass on cooling; distils between 240° and 245°, being for the most part decomposed at the same time. (Lauth and Grimaux.)

Trichloro-xylene, $C^8H^7Cl^3$, is easily produced by passing chlorine into xylene mixed with iodine, till the mass becomes solid. It boils at 254°—256°, and forms white silky needles, easily soluble in warm alcohol and benzene, sparingly in the same liquid when cooled. (Hollemann.)

Ethyl-xylene, $C^{10}H^{14} = C^8H^9(C^2H^5) = C^6H^3(CH^3)^2(C^2H^5)$, is produced (like ethyltoluene, p. 857) by the action of sodium on a mixture of monobromoxylene and ethylic bromide. It is a liquid having a specific gravity of 0·8783 at 30°, and boiling at 183°—184°. When warmed with nitrosulphuric acid, it is converted into a trinitro-compound, crystallising from alcohol in needles, and melting at 119°. By oxidation with chromic acid, it yields an acid resembling terephthalic acid, but more easily soluble in alcohol. (Fittig and Ernst, Ann. Ch. Pharm. cxxxix. 184.)

Methyl-xylene, $C^9H^{12} = C^8H^9(CH^3) = C^6H^3(CH^3)^3$, prepared in like manner, boils at 165°—166°, and unites with a small quantity of bromine (with evolution of hydrobromic acid), forming a solid bromide, which crystallises from alcohol in laminæ, melts at 73°, and is identical with bromide of cumene. The barium-salt of the sulpho-acid of methyl-xylene reacts also exactly like cumene-sulphate of barium. (Fittig and Ernst.)

Nitro-xylenes. (Müller, Zeitschr. Ch. Pharm. 1864, p. 161.—Beilstein, Ann. Ch. Pharm. cxxxiii. 45.—Fittig, *ibid.* cxxxiii. 48.—Glinzer and Fittig, *ibid.* cxxxvi. 307.—Deumelandt, Zeitschr. f. Chem. 1866, p. 21.)—When xylene (either from coal-naphtha, or prepared synthetically) is dissolved in cold fuming nitric acid, and water is added to the solution, a heavy oil separates out, consisting chiefly of mononitroxylene, but often depositing crystals of dinitroxylene after long standing.—*Mononitroxylene*, $C^8H^9(NO^2)$, is a liquid, and when pure distils without decomposition; on distilling the crude product, however, explosive decomposition takes place towards the end, arising from admixed dinitroxylene. Mononitroxylene boils at 240°. (Deumelandt.)

Dinitro-xylene, $C^8H^8(NO^2)^2$, is solid, and crystallises from dilute alcohol in highly lustrous crystals, which melt at 93°. From synthetically-prepared xylene, Fittig and Glinzer obtained, together with the dinitroxylene just described, an isomeric modification, melting at 123·5°.

Trinitro-xylene, $C^8H^7(NO^2)^3$, is easily produced by the action of a mixture of nitric and sulphuric acids upon xylene, by prolonged contact at ordinary temperatures, more quickly when heated. It is solid, and slightly soluble in cold alcohol; from boiling alcohol it crystallises in needles which melt at 177° (Beilstein). By the action of reducing agents it is converted into dinitroxylidine or nitroxylene-diamine (p. 1059).

The compound $C^8H^7(NO^2)^3$, described (iv. 382) as *trinitropetrol*, melts at 162°.

By the action of nitrosulphuric acid on synthetically-prepared xylene, and on the two modifications of dinitroxylene, Glinzer and Fittig obtained crystallisable trinitroxylene melting at 137°.

Ethylbenzene, $C^6H^5(C^2H^5)$, dissolves easily and with violent action in cooled fuming nitric acid, and water added to the solution throws down mononitro-ethylbenzene, $C^8H^9(NO^2)$, which distils without decomposition at 233°. At ordinary temperatures the nitration does not proceed any further; but on warming the liquid, or on dropping ethylbenzene into a warmed mixture of 2 vols. sulphuric and 1 vol. nitric acid, and adding water, dinitro-ethylbenzene, $C^8H^8(NO^2)^2$, separates as a non-distillable oil. This compound, boiled for an hour with nitrosulphuric acid, is converted into trinitro-ethylbenzene, $C^8H^7(NO^2)^3$, which is also a non-distillable oil.

Azo-xylene, C^8H^9N, or $C^{16}H^{18}N^2$.—Produced by the action of sodium-amalgam on nitroxylene. Crystallises in brick-red needles, which melt at 120°, and volatilise without decomposition. If the treatment with sodium-amalgam be further continued, colourless crystals are obtained, which dissolve very easily in alcohol and ether, and sublime even when the ethereal solution is evaporated: they probably consist of hydro-azoxylene, $C^{16}H^{20}N^2$. (Werigo, Zeitschr. f. Chem. 1864, p. 723; 1865, p. 312.)

XYLENE-DIAMINE. Syn. with XYLYLENE-DIAMINE (p. 1061).

XYLENE-SULPHOCHLORIDE. $C^8H^9SClO^2 = C^6H^3(CH^3)^2.SO^2Cl$. (Yssel de Scheffer, Zeitschr. f. Chem. 1865, p. 360.)—This compound is obtained, as a yellow non-distillable oil, by triturating xylene-sulphate of sodium with pentachloride of phosphorus, warming the mixture, and pouring the product into water. By the action of zinc and sulphuric acid, it is reduced to xylene-sulphydrate; when treated in ethereal solution with sodium-amalgam, it is converted into xylene-sulphurous acid.

XYLENE-SULPHURIC ACID. $C^8H^{10}SO^3 = C^8H^9.SO^3H = C^6H^3(CH^3)^2.SO^3H$. *Xylolsulphuric Acid. Sulphoxylolic Acid. Xylylsulphurous Acid.* (Church, Jahresb. 1855, p. 634.—Beilstein and Wahlforss, Ann. Ch. Pharm. cxxxiii. 38.—

Fittig and Glinzer, *ibid.* cxxxvi. 305.)—This compound (partly described as xylylsulphurous acid, p. 505) is produced by the action of strong sulphuric acid on xylene; if the mixture be warmed in the water-bath, and frequently shaken with fuming sulphuric acid, the action is quicker.

Xylene-sulphuric acid is crystallisable, and extremely soluble in water: by dry distillation it yields xylene.—Its *potassium-salt* is easily soluble in water and in alcohol, and crystallises from alcohol in silky laminæ.—The *barium-salt*, $C^8H^9.Ba''(SO^3)^2.H^2O$, forms spherical groups of shining scales, very soluble in water, and giving off their water of crystallisation over oil of vitriol.—The *calcium-*, *lead-*, and *copper-salts* are very soluble in water and in alcohol.

Amidoxylene-sulphuric Acid, $C^8H^8(NH^2).SO^3H = C^6H^2(NH^2)(CH^3)^2.SO^3H$.—*Xylidine-sulphuric Acid.*—Obtained by heating sulphate of xylidine with sulphuric acid. Crystallises from dilute aqueous solution in needles, and is so sparingly soluble in water that it may be precipitated from its salts.—The *barium-salt* forms nodules easily soluble in water. (Deumelandt, Zeitschr. f. Chem. 1866, p. 22.)

XYLENE-SULPHUROUS ACID. $C^8H^{10}SO^2 = C^8H^9.SO^2H = C^6H^3(CH^3)^2.SO^2H$.—A viscid uncrystallisable oil, produced by the action of sodium-amalgam on an ethereal solution of xylene-sulphochloride. (Otto, Zeitschr. f. Chem. 1866, p. 583.)

XYLENE-SULPHYDRATE. $C^8H^{10}S = C^8H^9.SH = C^6H^3(CH^3)^2.SH$. *Xylolsulphydrate. Xylylsulphydrate. Xylylic Mercaptan.* (Yssel de Scheffer, Zeitschr. f. Chem. 1865, p. 360.)—Produced by the action of zinc and sulphuric acid on xylene-sulphochloride. It is a colourless, strongly refracting oil, insoluble in water, soluble in alcohol and in ether. Boils at 213°.—Its *mercury-compound* crystallises from alcohol in white scales having a silky lustre.—The *lead-salt* is precipitated from alcoholic solutions as a powder of a fine yellow colour.—The *copper-* and *silver-salts* are pale-yellow unstable precipitates.

Xylene-sulphydrate is strongly attacked by bromine and by pentachloride of phosphorus, probably forming disulphide of xylene.

XYLENYL. Syn. with XYLYL (p. 1061).

XYLENYLAMINE.
XYLIDAMINE. } Syn. with XYLIDINE.

XYLIDINE. $C^8H^{11}N = C^8H^9(NH^2)$. *Amidoxylene. Amidoxylol.* (Church, Phil. Mag. [4], lx. 256.—Deumelandt, Zeitschr. f. Chem. 1866, p. 21.)—This base, homologous with aniline, toluidine, and cumidine, and isomeric with ethylaniline, dimethylaniline, and collidine, is produced by the action of sulphide of ammonium, ferrous acetate, or stannous chloride on nitroxylene. When this nitro-compound is treated with tin and hydrochloric acid, the whole solidifies on cooling to a crystalline mass, consisting of a compound of hydrochlorate of xylidine with stannous chloride, which, by recrystallisation from strong hydrochloric acid, may be obtained in large scaly crystals. By decomposing this compound with sulphuretted hydrogen, and evaporating the filtrate, crystallised hydrochlorate of xylidine is obtained, which forms an easily decomposible double salt with platinic chloride.

Free xylidine may be obtained by distilling the hydrochlorate with dry soda—or (better) by reducing nitroxylene with iron and acetic acid, and distilling the product with excess of soda-ley. The base thus obtained may be combined with hydrochloric acid, and precipitated by potash from this salt, after it has been purified by recrystallisation.

Xylidine is a colourless liquid, heavier than water, and boiling at 214° to 216°.—*Nitrate of xylidine* crystallises in white silky laminæ; the *sulphate* and *oxalate* are also crystallisable.

Dinitroxylidine, $C^8H^7(NO^2)^2.NH^2$, is produced, together with nitroxylylene-diamine (p. 1061), by the action of ammonium-sulphide on trinitroxylene (Beilstein, Ann. Ch. Pharm. cxxxiii. 45). It is identical with the yellow base obtained by Bussenius and Eisenstück as a bye-product in the reduction of trinitroxylene (trinitropetrol) from the petroleum of Sehnde (iv. 382, footnote). On dissolving out the nitroxylylene-diamine with dilute hydrochloric acid, the dinitroxylidine remains behind, and must be freed from sulphur by recrystallisation from alcohol. It is yellow, insoluble in water, alkalis, and dilute acids, soluble in hot concentrated acids; but is separated, in the pulverulent form, from these solutions on addition of water. From alcoholic solution it separates, by very slow cooling, in needle-shaped crystals, which melt at 191°—192°.

XYLIDINE-SULPHURIC ACID. Syn. with AMIDOXYLENE-SULPHURIC ACID.

XYLITE. This name is given by Hermann (Bull. Soc. d. Sc. nat. de Moscou, i. 247) to a mineral containing 44 per cent. SiO^2, 38·22 Fe^2O^3, 6·1 CuO, 4·8 MgO, 0·68 CuO, and 4 44 water, forming finely fibrous masses resembling mountain-wood, of specific gravity 2·935.

XYLITE of Weidmann and Schweizer. Syn. with Lignone (iii. 694).

XYLOBALSAMUM. The commercial name of the odoriferous wood of *Amyris gileadensis*, which yields Mecca balsam (i. 495).

XYLOCHLOERIC ACID. A term applied by Fordos (Compt. rend. lvii. 50) to the green colouring-matter of decayed wood, which may be extracted by chloroform.

XYLOCHLORE. A mineral found in a fossil tree-stem from the volanic tufa near Husavik in Iceland, forming olive-green quadratic pyramids, and containing 52·07 SiO^2, 1·54 Al^2O^3, 20·57 CaO, 0·33 MgO, 3·4 FeO, 0·55 Na^2O, 3·77 K^2O, and 17·14 water (Sartorius v. Waltershausen, Vulcan. Gest. Islands, p. 297). Kenngott (J. pr. Chem. lxxxix. 455) has shown that it is an altered form of apophyllite.

XYLOCRYPTITE. A mineral apparently related to Scheererite, occurring in yellow waxy crystalline particles on lignite. (Becquerel.)

XYLOÏD. Löwig's name for the radicle xylyl, C^8H^9.

XYLOÏDIC ACID. See the next article.

XYLOÏDIN. $C^6H^9NO^7 = C^6H^9(NO^2)O^5$. *Pyroxam. Nitramidin. Explosive Starch.* (Braconnot, Ann. Ch. Phys. [2], lii. 290.—Liebig, Ann. Ch. Pharm. vii. 249.—Payen, N. Ann. Sc. nat. Bot. x. 161.—Pelouze, Compt. rend. vii. 713; xxiii. 890.—Gladstone, Mem. Chem. Soc. iii. 412.—Bouijs-Ballot, Ann. Ch. Pharm. xlv. 47.—Béchamp, Ann. Ch. Phys. [3], xlvi. 338; lxiv. 311.—Gm. xv. 106.)—This compound, discovered by Braconnot in 1833, is produced by the action of strong nitric acid upon starch. To prepare it, starch is triturated in a thick porcelain mortar (to prevent rise of temperature) with 5 to 8 pts. of fuming nitric acid, till it is reduced to a transparent semifluid mass, without evolution of gas; and 20 to 30 pts. of water are then added, whereupon the xyloïdin is precipitated as a white granular mass, while a small quantity of starch remains in solution. If the action of the acid be too much prolonged, the liquid becomes coloured, nitric oxide is given off, and no precipitate is obtained on subsequent addition of water: but the liquid then contains a deliquescent uncrystallisable acid (called *xyloïdic acid*, but probably identical with saccharic acid). (Pelouze, Béchamp.)

To purify the xyloïdin, it is dissolved, after washing and drying, in a mixture of 10 pts. glacial acetic acid, ($C^2H^4O^2$), and 1 pt. of the dihydrated acid, ($C^2H^4O^2.2H^2O$), and the solution is filtered and evaporated. 100 pts. starch thus treated yield from 128 to 130 pts. of xyloïdin. (Béchamp.)

Xyloïdin is a white, inodorous, and tasteless powder, which does not redden litmus. It is insoluble in water, alcohol, ether, chloroform, ethylic acetate, acetone, and benzene; dissolves in glacial acetic acid to a thick mucilage, more easily, according to Béchamp, on addition of $\frac{1}{10}$ of the dihydrated acid; the solution coagulates on addition of water. In boiling water, xyloïdin cakes together without dissolving.

Xyloïdin when struck decomposes with detonation, but not so violently as guncotton. It melts when heated, and takes fire at 180°, burning brightly, and leaving a carbonaceous residue. Gladstone found that a sample which had been kept for six years, decomposed suddenly, with evolution of gas containing a large proportion of hydrocyanic acid, and after some weeks a somewhat tenacious residue remained behind.

Bromine does not act upon xyloïdin.—*Iodine* colours it yellow.—Strong *nitric acid* dissolves it, with decomposition, after some time.—Strong *sulphuric acid* dissolves it with blackening, and on adding water the xyloïdin separates out: dilute sulphuric acid does not dissolve it.—In strong *hydrochloric acid* it dissolves without decomposition, and is precipitated by water in its original state.—It is partially dissolved by *potash*.—*Ferrous salts* decompose it, with evolution of nitric oxide and production of soluble starch:

$$\underset{\text{Xyloïdin.}}{2C^6H^9(NO^2)O^5} + 6FeCl^2 + H^2O = Fe^2O^3 + 2Fe^2Cl^6 + 2NO + \underset{\text{Starch.}}{2C^6H^{10}O^5}.$$

The starch may be precipitated from the resulting solution by alcohol, and thus obtained in a state of purity.

Soluble Xyloïdin, Isoxyloïdin, or *Isonitramidin.*—This modification of xyloïdin is obtained by treating starch with excess of strong nitric acid (10 to 12 pts.), precipitating the yellow gummy solution with water, dissolving the dried precipitate in ether-alcohol, and evaporating the filtrate. The product thus obtained resembles xyloïdin in composition, and in many of its properties, but is distinguished therefrom by being perfectly soluble in pure alcohol, wood-spirit, acetone, ether, a mixture of ether and alcohol, and in ethylic acetate; in alcohol of 95 per cent. it is insoluble. (Béchamp, Ann. Ch. Phys. [3], lxiv. 320.)

Nitroxyloïdin, or *Dinitramidin*, $C^6H^8(NO^2)^2O^5$, is produced, also in a more soluble and less soluble modification, by the action of strong sulphuric acid on xyloïdin or isoxyloïdin. To prepare it, 1 pt. of dry starch is dissolved in 12 pts. fuming nitric acid, and the solution (filtered, if necessary, through pounded glass) is placed in a freezing mixture, and quickly mixed with 8 pts. oil of vitriol; the soft white mass thereby separated is quickly mixed with a large quantity of cold water; and the product, which is a white powder resembling xyloïdin, is well washed, and dried in a hot-air chamber. This product is chiefly a mixture of nitroxyloïdin and isonitroxyloïdin, which may be separated from one another by digestion with alcohol of 96 per cent., first in the cold, then at 40°, whereby the isonitroxyloïdin is dissolved, and the nitroxyloïdin remains behind.

Nitroxyloïdin is a white easily pulverised mass, which decomposes much more readily than xyloïdin, and is reduced by ferrous salts in the same manner as the latter, yielding soluble starch. It is insoluble in water and in alcohol, but soluble in pure ether, and in alcoholised ether; soluble in glacial acetic acid, but insoluble in a mixture of the glacial and dihydrated acid, exhibiting, in this respect, exactly the opposite relation to xyloïdin.

Isonitroxyloïdin is insoluble in water, soluble in alcohol of 96 per cent., dissolves with difficulty in ether, but easily in a mixture of ether and alcohol. It is even more prone to spontaneous decomposition than the less soluble modification.

XYLOL. Syn. with XYLENE.

XYLOLITE. Syn. with mountain-wood, or ligniform asbestos (i. 415).

XYLOLSULPHURIC ACID. Syn. with XYLENE-SULPHURIC ACID (p. 1058).

XYLOLSULPHYDRATE. Syn. with XYLENE-SULPHYDRATE (p. 1059).

XYLONES, CHLORINATED. This term was applied by Gorup-Besanez (Ann. Ch. Pharm. lxxxvi. 237), to various chlorinated products, formed by treating the creosote of beechwood tar with potassic chlorate and hydrochloric acid: they are not, however, related in any way to xylene.

XYLORETIN. $C^{10}H^{16}O$.—A crystalline resin, isomeric or polymeric with camphor, occurring in fossil pine-trunks. It is insoluble in water, easily soluble in alcohol and ether, and crystallises from the ethereal solution in white masses; melts at 165°; cannot be volatilised without decomposition. It unites with bases, without separation of water. Heated with *potassium*, it gives off hydrogen, and forms a potassium-compound, which dissolves in alcohol and crystallises therefrom.

XYLOSTEIN. See the next article.

XYLOSTEUM. The berries of the fly honeysuckle (*Lonicera Xylosteum*) were formerly used medicinally as *Baccæ xylostei*: they are said to be narcotic. They contain 86·4 per cent. water, 2·3 substances soluble in ether, 6·2 soluble in alcohol, and 2·9 soluble in water. The fresh berries yield 1 per cent. ash, containing (in 100 pts.) 22·8 K^2O, 9·5 Na^2O, 23·5 CaO, 8·2 MgO, 0·8 Al^2O^3 and Fe^2O^3, 4·8 SO^3, 16·2 P^2O^5, 2·9 SiO^2, 1·3 Cl, and 10·0 CO^2 (Enz, Chem. Centralbl. 1856, p. 393).—According to Hübschmann (Arch. Pharm. lxxxv. 250), the berries contain a peculiar, non-volatile, bitter principle, xylostein, soluble in alcohol and ether, insoluble in water. According to Enz, this body is a glucoside, yielding sugar when decomposed by acids.

XYLOTIL. Syn. with MOUNTAIN-WOOD (i. 415).

XYLYL. C^8H^9.—A monatomic radicle, homologous with phenyl and tolyl, which may be supposed to exist in xylene ($C^8H^9.H$) and its derivatives.

XYLYLAMINE. This name belongs to a base, $C^8H^9.H^2.N = C^6H^4\left\{\begin{matrix}CH^3\\CH^2(NH^2)\end{matrix}\right.$ (not yet obtained), related to benzylamine, $C^7H^7.H^2.N$ (p. 807), in the same manner as xylidine, $C^8H^9(NH^2) = C^6H^3(NH^2)\left\{\begin{matrix}CH^3\\CH^3\end{matrix}\right.$ to toluidine, $C^6H^4(NH^2).CH^3$ (p. 852).

XYLYLATES. See XYLYLIC ACID (p. 1062).

XYLYLENE. C^8H^8.—A diatomic radicle related to xylyl, C^8H^9, in the same manner as ethylene to ethyl.

XYLYLENE-DIAMINE, $C^8H^{12}N^2 = \begin{matrix}(C^8H^8)''\\H^4\end{matrix}\Big\} N^2$, or *Diamido-xylene*, $C^8H^8(NH^2)^2$, is formed by reducing dinitroxylene with tin and hydrochloric acid; its hydrochlorate, treated with bromine, yields the hydrochlorate of bromoxylylene-diamine, $C^8H^7Br.(NH^2)^2$.

Nitroxylylene-diamine, or *Nitro-diamidoxylene*, $C^8H^7(NO^2)(NH^2)^2$, is the compound already described as nitropetrol-diamine, which Bussenius and

Eisenstück obtained by reducing the so-called trinitropetrol with sulphide of ammonium (iv. 382).

XYLYLIC ACID. $C^9H^{10}O^2 = C^6H^3(CH^3)^2.CO^2H$. (Kekulé, Bull. Soc. Chim. 1866, ii. 47.—Hirzel and Beilstein, *ibid.* 1867, i. 345.)—This acid, homologous with benzoic and toluic acids, is produced:—1. By the action of sodium and carbonic anhydride on bromoxylene (Kekulé):

$$\underset{\text{Bromo-xylene.}}{C^8H^9Br} + Na^2 + CO^2 = NaBr + \underset{\text{Xylylate of sodium.}}{C^8H^9.CO^2Na.}$$

The process is conducted as for the preparation of toluic acid from toluene (p. 862), the bromoxylene being diffused through a hydrocarbon boiling at about 120°.—2. By oxidising cumene (C^9H^{12}) with potassic bichromate and sulphuric acid, or (better) with dilute nitric acid. (Beilstein and Kögler, Ann. Ch. Pharm. cxxxvii. 317; Jahresb. 1865, p. 559.)

Cumene oxidised with dilute nitric acid yields first xylylic acid, and afterwards insolinic acid, [$C^9H^8O^4 = C^6H^3(CH^3)(CO^2H)^2$]. To prepare xylylic acid, cumene is treated with nitric acid diluted with twice its volume of water; and the acid product is treated with tin and hydrochloric acid, to decompose the nitro-acids formed at the same time. On distilling the product with water, xylylic acid passes over, while insolinic acid remains behind. If the cumene employed is not pure, an oily product distils over at the same time; in that case the receiver must be changed as soon as crystalline xylylic acid begins to pass over. (Hirzel and Beilstein.)

Xylylic acid is insoluble in cold water (Kekulé); very slightly soluble (Hirzel and Beilstein). It dissolves sparingly in boiling water, and separates on cooling in white needles; dissolves very easily in alcohol and ether (Kekulé). According to Hirzel and Beilstein, it melts in boiling water; in the dry state it melts at 103°, and boils at 273°. It sublimes easily in needles (Kekulé). Xylylic acid is quickly oxidised by chromic acid, and converted into insolinic acid, $C^9H^8O^4$. (Hirzel and Beilstein.)

Xylylate of Barium, $(C^9H^9O^2)^2Ba''.4H^2O$, crystallises in shining colourless laminæ.—The *calcium-salt*, $(C^9H^9O^2)^2Ca''.3H^2O$, forms stellate groups of shining needles.—The *ethylic ether*, $C^9H^9(C^2H^5)O^2$, is an aromatic oil, boiling at 233°. (Hirzel and Beilstein.)

Alphaxylylic Acid, $C^9H^{10}O^2 = C^6H^4\left\{\begin{matrix}CH^3\\CH^2.CO^2H\end{matrix}\right.$ (Vollrath, Zeitschr. f. Chem. 1866, p. 488; Jahresb. 1866, p. 605.)—This acid, homologous with alphatoluic acid (p. 863), is formed by boiling toluylic chloride, C^8H^9Cl (p. 870), in alcoholic solution with cyanide of potassium, and then with potash:

$$\underset{\text{Toluylic chloride.}}{C^6H^4\left\{\begin{matrix}CH^3\\CH^2Cl\end{matrix}\right.} + CNK + 2H^2O = KCl + NH^3 + \underset{\text{Alphaxylylic acid.}}{C^6H^4\left\{\begin{matrix}CH^3\\CH^2.CO^2H.^*\end{matrix}\right.}$$

It may be precipitated from the resulting solution by an acid, and, when purified by boiling with milk of lime, crystallises in broad needles, having a satiny lustre, melting at 42°, and dissolving very readily in water.

XYLYLIC ACETATE, CHLORIDE, &c. Syn. with TOLUYLIC ACETATE, CHLORIDE, &c. (pp. 870, 871).

XYLYLIC ALCOHOLS. $C^8H^{10}O$.—This formula may include several isomeric compounds, but only three have hitherto been investigated with any approach to accuracy:—

1. The compound described (p. 869) as toluylic alcohol, $C^8H^9.OH$ or $C^6H^3(CH^3)^2.OH$, which would be better called xylylic alcohol, inasmuch as it is obtained directly from the chloride, $C^8H^9.Cl$ (chloride of xylyl), produced by the action of chlorine on xylene at high temperatures. This alcohol is the homologue of benzylic or tolylic alcohol, $C^7H^7.HO$ (i. 578).

2. The compound called phlorol, phloretol, or phlorylic alcohol, which Hlasiwetz obtained by distilling barium-phloretate with lime (iv. 493). This compound is a true homologue of phenol, probably ethyl-phenol, $C^6H^4(C^2H^5).OH$.

3. The "xylylic phenol," mentioned by H. Müller (Zeitschr. f. Chem. 1865, p. 271) as occurring in coal-tar. This is probably dimethyl-phenol, $C^6H^3(CH^3)^2.OH$, inasmuch as products obtained by dry distillation have hitherto been found to contain only methyl-derivatives of benzene. The portion of aloïsol (the product obtained by distilling aloes with lime, i. 148), which is soluble in potash, has also, according to

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[*] This is the formula of insolinic acid originally given by Hofmann (p. 725). According to Hirzel and Beilstein, insolinic acid is very much like terephthalic acid, but dissolves very easily in boiling water. It does not yield any higher oxidation-products when treated with chromic acid.

Rembold (Ann. Ch. Pharm. cxxxviii. 186), the composition of a xylylic alcohol, and is, perhaps, identical with the last mentioned.

XYLYLIC MERCAPTAN. Syn. with Xylene-sulphydrate (p. 1059).

XYLYLSULPHAMIC ACID, $C^8H^{11}NSO^3$, is produced by heating sulphate of xylidine with sulphuric acid, and crystallises in needles very slightly soluble in cold water.—Its *barium-salt*, $(C^8H^{10}NSO^3)^2Ba''$, is very soluble, and crystallises in nodular groups. (Deumelandt, Bull. Soc. Chim. 1866, ii. 211.)

XYLYLSULPHUROUS ACID. Syn. with Xylene-sulphuric Acid (p. 1058).

XYLYLSULPHYDRATE. Syn. with Xylene-sulphydrate (p. 1059).

Y

YABICOJA. An ore occurring, with atacamite and quartz, in the district of Tarapaca in Peru. (Leonh. Jahrb. p. 243.)

YAM. See Dioscorea (ii. 335).

YANOLITE, or **YANTHOLITE.** Syn. with Axinite (i. 477).

YEAST. See Fermentation (ii. 629).

YELLOW COPPER-ORE. Syn. with Copper Pyrites (ii. 77).

YELLOW COPPERAS. Syn. with Botryogen (i. 651).

YELLOW DYES. See Dyeing (ii. 356).

YELLOW LEAD-ORE. Native molybdate of lead, or wulfenite. (See Molybdenum, iii. 1039.)

YELLOW METAL. An alloy of 60 pts. copper and 40 pts. zinc; also called Muntz's metal. (See Copper, Alloys of, ii. 49.)

YELLOW OCHRE. See the next article.

YELLOW PIGMENTS. The yellow pigments mostly employed as artists' colours are *sulphide of cadmium* (i. 706), *gamboge* (ii. 770), *Indian yellow*, which consists mainly of euxanthate of magnesium (ii. 609), and *yellow ochre*, which consists of clay or marl coloured with ferric oxide.—*Chrome-yellow*, or neutral chromate of lead, is used chiefly for carriage-painting; also for colouring wall-papers, and as an ingredient in yellow varnishes; it is never used alone, but always mixed with chromate of calcium or barium, or sulphate of lead. A mixture of chromate of lead with the sulphates of lead and calcium constitutes *Cologne yellow*. Other yellow lead-salts are also used as pigments, chiefly for house-decoration and paper-staining—viz., certain oxychlorides of lead (iii. 556), known as *Turner's yellow, Cassel yellow*, &c.; a basic sulphate, $PbSO^4.PbO$, known in France as *jaune paille mineral*, and prepared by fusing a mixture of neutral sulphate and oxide of lead; *Naples yellow*, a basic antimoniate of lead (i. 326), used as an artists' colour, in oil-painting; and less frequently, *iodide of lead*, which has a fine colour, but is somewhat fugitive; and *arsenate of lead*, which is objectionable on account of its poisonous character. All these lead-yellows cover well, but have the inconvenience of turning brown or black on exposure to sulphuretted hydrogen.—*Chromate of zinc*, prepared by precipitation, has a fine colour, much like that of chromate of lead, and is not affected by sulphuretted hydrogen.—The *chromates of barium* and *calcium* are used for colouring paper-hangings, also for mixing with chromate of lead. (Lefort, *Chimie des Couleurs*, 1855.)

YELLOW PODS. The pods of *Gardenia grandiflora*, which yield crocin (ii. 108).

YELLOW TELLURIUM. Syn. with Sylvanite (p. 647).

YENITE. Syn. with Lievrite (iii. 589).

YERBA MATÉ. Syn. with Paraguay Tea (iv. 349).

YPADU-PLANT. Syn. with Coca (i. 1059).

YTTERBITE, YTTERITE. Syn. with Gadolinite (ii. 757).

YTTRIA. Oxide of yttrium (p. 1064).

YTTRITE. Syn. with Gadolinite.

YTTRIUM. *Symbol*, Y; *Atomic weight*, 61·7 (Bahr and Bunsen); 71·4 (Delafontaine).—An element belonging to the class of earth-metals, but existing only in a few very rare minerals. Gadolin, in 1794, obtained from the ytterbite or gadolinite of Ytterby in Sweden, a peculiar oxide resembling lime and alumina. Ekeberg, in 1797, confirmed these results, and named the earth yttria. In a subsequent examination of this earth, which in the meantime had been investigated also by Klaproth and Vauquelin, Ekeberg found that his yttria contained glucina. Berzelius, in 1819, found that it also contained oxide of cerium (associated, according to subsequent investigations, with the oxides of lanthanum and didymium). Scheerer, in 1842, pointed out that yttria, even when freed from the oxides of the cerium-metals, probably still contained another oxide; and Mosander, in 1843, by a careful examination of crude yttria, concluded that it was a mixture of three earths—which he named yttria, terbia, and erbia—separable by their different degrees of basicity. Subsequent experiments by different chemists have, however, thrown considerable doubt on the separate existence of the second of these earths; and the recent very careful experiments of Bahr and Bunsen, already referred to under TERBIUM (p. 721), seem to have shown conclusively that crude yttria, when completely freed from the oxides of cerium, lanthanum, and didymium, may be separated into two earths, yttria and erbia, without any trace of a third, the so-called terbia. The method of effecting this separation, and obtaining pure salts of erbium and yttrium, has been already described (p. 721).

Metallic yttrium is obtained by igniting chloride of yttrium with potassium. It is described by Berzelius as a blackish-grey powder, consisting of small metallically lustrous scales, becoming brittle, and acquiring the colour and lustre of iron under the burnisher. The metal thus characterised was, however, a mixture of yttrium and erbium; pure yttrium has not yet been prepared.

Yttrium is a diatomic metal, and forms but one series of compounds, YCl^2, YO, &c. It unites directly at high temperatures with chlorine, oxygen, and sulphur, and probably with other metalloïds.

Bromide of Yttrium is obtained, by evaporating a solution of yttria in hydrobromic acid, as a very deliquescent saline mass.

Chloride of Yttrium is a non-volatile compound, obtained by heating yttrium in chlorine-gas.

The *hydrated chloride*, obtained by leaving a solution of yttrium in hydrochloric acid to evaporate, is a saline mass which slowly deliquesces.

Fluoride of Yttrium occurs, together with the fluorides of cerium and calcium, in varying proportions, as yttrocerite, a mineral found at Finnbo and Broddbo in Sweden; at Amity, New York, and in Massachusetts, forming violet-blue, crystallo-granular, and earthy masses, imbedded in quartz; in smaller quantity also as fluocerite (ii. 609). By mixing a solution of yttrium-chloride with potassium-fluoride, hydrated yttrium-fluoride is obtained as a white amorphous precipitate, having an astringent taste; it reddens litmus, is insoluble in water and in aqueous hydrofluoric acid; when heated in a close vessel, it leaves the anhydrous fluoride.

Borofluoride of Yttrium, obtained by double decomposition, is insoluble in water, but soluble in acids, even in excess of fluoboric acid, and crystallises on evaporating the solution.—The *silicofluoride* exhibits similar properties.

Iodide of Yttrium is prepared like the bromide, and is likewise very deliquescent.

Oxide of Yttrium,—Yttria,—obtained by igniting the oxalate, is a soft nearly white powder, which, when ignited, glows with a pure white light, and yields a spectrum not containing any bright bands, like that of erbia (p. 722). It does not unite directly with water, but is precipitated as a hydrate by alkalis from solutions of yttrium-salts. It dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids, forming colourless solutions which do not exhibit an absorption-spectrum.

Oxygen-salts.—Basic Nitrate of Yttrium, $Y''(NO^3)^2.Y''O.3H^2O$, prepared like the corresponding erbium-salt (p. 722), crystallises in colourless deliquescent needles.—The *oxalate*, $C^2Y''O^4.H^2O$, is a soft white powder, which does not give off its water till heated nearly to the temperature at which it decomposes.—The *sulphate*, $3Y''SO^4.8H^2O$, forms colourless well-defined crystals, isomorphous with the corresponding erbium- and didymium-salts, and exhibiting the same characters as the erbium-salt when heated, and when dissolved in water. (Bahr and Bunsen.)

Selenide of Yttrium is obtained, according to Wöhler, by fusing yttria with selenium, as a black substance which is insoluble in water, and gives off selenhydric acid when treated with dilute acids (Wöhler). Selenide of ammonium precipitates yttrium-salts. (Berzelius.)

Sulphide of Yttrium is produced, with ignition, when yttrium is heated in sulphur-vapour; also when yttria is heated in vapour of carbonic disulphide. It is a grey pulverulent body, which is not decomposed by water, but gives off sulphydric acid when treated with dilute acids. (Wöhler.)

Detection and Estimation of Yttrium.

Yttrium-salts are colourless, and resemble those of thorinum (p. 786), in their behaviour before the blowpipe, and in most of their reactions in solution. Yttrium is distinguished from thorinum by the solubility of its ignited oxide in hydrochloric acid, by the non-volatility of its anhydrous chloride, and by the solubility of yttrio-potassic sulphate (precipitated from yttrium-solutions by potassic sulphate), in excess of potassic sulphate. The solubility of ignited yttria in hydrochloric acid serves also to distinguish yttria from alumina and zirconia; it is further distinguished from alumina and from glucina by its insolubility in potash. The precipitation of yttria by alkalis is not prevented by the presence of tartaric acid (distinction from alumina, glucina, thorina, and zirconia), the yttrium being slowly but completely precipitated as tartrate. Acidulated solutions of yttrium-salts do not alter the colour of turmeric-tincture (distinction from zirconium).

For quantitative estimation, yttrium is precipitated as hydrate by *ammonia* or *potash*, or as oxalate by *oxalic acid*; the precipitate in either case leaves anhydrous yttria when ignited. If potassium-salts are present in the solution, the precipitate formed by oxalic acid consists of yttrio-potassic oxalate, which, when ignited, leaves a mixture of yttria and potassic carbonate. This may be dissolved in hydrochloric acid, and the yttria precipitated by ammonia.

Yttrium may be separated from iron, existing in solution as ferric salt, by precipitating the iron as ferric oxide with *succinate of ammonium*, or (better) with *carbonate of barium*.—From the cerium-metals, yttrium is separated by immersing in the solution an excess of solid *sulphate of potassium*; the yttrio-potassic sulphate then dissolves, while the double sulphates of potassium and the cerium-metals remain undissolved.—From aluminium and glucinum, yttrium may be separated by precipitation with *oxalic acid*, or by adding *tartaric acid* in excess, and precipitating the yttrium with *ammonia*.—To separate yttrium from magnesium, the solution is mixed with excess of ammonium-salt, and the yttria precipitated by *ammonia*.

In all these modes of precipitation, yttrium is thrown down, together with erbium. The only satisfactory method yet given for separating these metals one from the other is that of Bahr and Bunsen, already described; and even this is very far from affording the means of determining the relative quantities of the two when mixed together.

The atomic weight of yttrium is determined by the analysis of its sulphate. From the anhydrous salt, $Y''SO^4$, or $YO.SO^3$, Bahr and Bunsen obtained, in two determinations, 49·30 and 49·24 per cent. YO, 50·69 and 50·76 per cent. SO^3: whence Y = 61·7. Delafontaine obtained, as a mean of three determinations, 48·23 per cent. OY, giving Y = 74·5.

YTTROCERITE. A mineral consisting of fluoride of yttrium mixed with the fluorides of cerium and calcium (p. 1064).

YTTROCOLUMBITE. Syn. with YTTROTANTALITE.

YTTROILMENITE. Uranoniobate of yttrium and iron: syn. with SAMARSKITE (iv. 54).

YTTROTANTALITE. Tantalate of yttrium, found at Ytterby in Sweden (p. 668).

YTTROTITANITE. *Keilhauite.*—A silicotitanate containg lime, yttria, ferric oxide, and alumina, with small quantities of other bases. It occurs at Buö, near Arendal in Norway, in monoclinic crystals, isomorphous with sphene (p. 398), more or less translucent, having a brownish-red to dark-brown colour, with yellowish streak; waxy lustre on the neutral faces, vitreous on the cleavage-faces. Hardness = 6 to 7; specific gravity = 3·5 to 3·7. Before the blowpipe it behaves, for the most part, like sphene.

Analyses: *a*, *b*, by A. Erdmann (Berz. Jahresb. xxv. 328).—*c*, by D. Forbes (Ed. N. Phil. J. [new series], i. 62).—*d*, *e*, by Rammelsberg (Pogg. Ann. civ. 296):

	SiO^2.	TiO^2.	Fe^2O^3.	Al^2O^3.	YO.	CeO.	CaO.	MnO.		Loss by ignition.	
a. . .	30·00	29·01	6·35	6·09	9·62	0·32	18·92	0·67	. .	. .	= 100·98.
b. . .	29·45	28·14	6·48	5·90	9·74	0·63	18·68	0·86	. .	. .	= 99·88.
c. . .	31·33	28·84	7·63	8·23	4·78	0·28	19·56	. .	0·32 GO	. .	= 100·97.
d. (cryst.)	29·48	26·67	6·75	5·45	8·16	. .	20·29	. .	0·94 MgO 0·60 K^2O	0·54	= 98·88.
e. (massive)	28·50	27·04	5·90	6·24	12·08	. .	17·15	3·59	. .	. .	= 100·50.

If the ferric oxide and alumina be regarded as acid constituents, the mineral may be represented by the formula $3M''O(Al^2O^3;Fe^2O^3) + 15M^2O.2(SiO^2;TiO^2)$, analogous to that of sphene. (Rammelsberg.)

YU. The name of a mineral highly prized in China, and, according to Abel-Remusat (Berz. Jahresb. v. 223), identical with *jade nephritique* (? nephrite). It has a specific gravity of 2·9 to 3·4, scratches glass, and is scratched by quartz.

Z

ZACOTINGA. A specular iron-ore from Porpez, in Brazil.

ZAFFRE. An impure oxide of cobalt, produced by imperfectly roasting cobalt-ore mixed with 2 or 3 pts. of siliceous sand.

ZALA. Syn. with BORAX.

ZAMBONI'S PILE. A name sometimes applied to the dry pile. (See ELECTRICITY, ii. 423.)

ZAMTITE. A hydrated carbonate of nickel from Spain, probably identical with texasite or emerald-nickel (i. 789).

ZANTHOPICRIN. Syn with XANTHOPICRITE (p. 1053).

ZEAGONITE. A calcio-aluminic silicate allied to abrazite (i. 1), but crystallising in trimetric forms, whereas abrazite is dimetric. It occurs in the lava of Capo di Bove, near Rome, in small crystals, which are combinations of the prisms $\infty\breve{P}\infty$ and $\infty\bar{P}\infty$, with a pyramid, or in irregular and spherical groups. It is transparent to semitranslucent, with a vitreous lustre, white to bluish-white colour, and white streak. Hardness = 5·0. Specific gravity = 2·213. Before the blowpipe it becomes opaque, then splits, and melts to a transparent or whitish tumefied glass. Hydrochloric acid dissolves it, with separation of gelatinous silica.

Analyses: *a*, by v. Kobell (J. pr. Chem. xviii. 205);—*b*, by Marignac (Ann. Ch. Phys. [3], xiv. 41):

	SiO^2.	Al^2O^3.	CaO.	K^2O.	H^2O.		
a.	42·72	25·77	7·60	6·28	17·66	=	100·03
b.	43·64	24·39	6·92	10·35	15·05	=	100·35

These analyses do not agree very closely, but the formula of the mineral is probably that deduced from the second, viz. $(CaO;K^2O)SiO^2 + (Al^2O^3.2SiO^2) + 4aq$.

ZEASITE. A dark-coloured opal from Mexico, exhibiting a green and red play of colours.

ZEDOARIN. See the next article.

ZEDOARY. *Radix zedoariæ.*—The root of *Curcuma zedoaria*, a scitaminaceous plant, growing in Bengal, Java, and Madagascar. It has a camphoric odour, and an aromatic somewhat bitter taste. Contains, according to Bucholz (Repert. Pharm. xx. 376), volatile oil, a bitter soft resin, a bitter extractive matter, gum, starch, &c. The oil is turbid, whitish-yellow, and viscid, has a camphoric taste and smell, and consists of two oils, one lighter, the other heavier, than water. Trommsdorff obtained from the root a substance which he called zedoarin, but did not further describe.

ZEILANITE. Syn. with PLEONAST or FERRUGINOUS SPINEL (p. 400).

ZEIODELITE. This name is applied to a mixture obtained by stirring 24 pts. of finely-pounded glass into 20 pts. of sulphur. It is recommended as a cement for stone and metal, for the taking of casts instead of gypsum or sulphur; as a material for bookbinding letters, stereotype plates, statues, and whetstones; and even as a substitute for lead in the construction of vitriol chambers. It may be tinted at pleasure, by addition of colouring-matter. (A. Vogel, Buch. N. Repert. xii. 294.)

ZEA MAÏS. Maize or Indian-corn. On the composition of the grain of this plant, see CEREALS (i. 225, 227).

ZEIN. A nitrogenous substance obtained from maize-flour (Gorham, Berz. Jahresb. ii. 124.—Stepf, J. pr. Chem. lxxvi. 88; Jahresb. 1859, p. 593).—Maize-flour, when washed with water, does not yield a mass resembling the gluten of wheat.

ZEOLITES. A generic name of hydrated double silicates in which the principal bases are alumina and lime, the latter being often more or less displaced by ferrous oxide, magnesia, and alkalis. They boil up when heated on charcoal before the blowpipe, and are dissolved by acids, leaving gelatinous silica. Many of them form very fine crystals. Natrolite is sometimes called *feather zeolite*; stilbite, *foliated zeolite*; scolecite, *needle zeolite*; apophyllite, *pyramidal zeolite*; laumontite, *efflorescing zeolite.*

ZEOTIN-SALT. Syn. with NITRATE OF SODIUM (iv. 105).

ZER [illegible] **T** This name appears to be applied to two different roots—

namely, that of *Zingiber Cassumanar*, a scitaminaceous plant indigenous in Coromandel and in Java; and that of *Zingiber Zerumbet*, imported from Calcutta and Java. Both have an aromatic odour and a bitter taste. According to Luca (Berl. Jahrb. 1798, iv. 214), zerumbet-root (the particular kind is not stated) contains an essential oil having a camphoric odour, a bitter and soapy extractive matter, bitter resin, gum, &c.

ZINC. Synonyms: *Spelter. Spiauter. Zincum.* Atomic weight, 65; Symbol, Zn.—The ore of zinc, called calamine or cadmia,—but not the pure metal—was known to the ancient Greeks, and used in the manufacture of brass. Metallic zinc was first mentioned by Paracelsus; it was for a long time imported from the East, but since the middle of the eighteenth century, it has been prepared in Europe.

Zinc occurs in considerable abundance as carbonate, forming the ore called calamine; as silicate, or siliceous calamine; as sulphide or blende, and as oxide or red zinc-ore; in smaller quantities also as aluminate, arsenate, phosphate, and sulphate. Quite recently, native metallic zinc has been found at Victoria, in Australia. Zinc is likewise found in the ash of a species of violet, *Viola calaminaria*, which grows on the dead heaps at the calamine mines in Rhenish Prussia.

Metallurgy of Zinc.—The ores from which the metallic zinc of commerce is extracted are four in number—viz., blende, red oxide, calamine, and siliceous calamine. All these are subjected to a preliminary calcination before being smelted.

In the case of blende, this calcination is necessary for the purpose of expelling the sulphur, and converting the sulphide into a more or less pure oxide of zinc. The calamine, on calcination, loses its carbonic acid, together with some moisture; and the red oxide and siliceous calamine, besides losing water, become more porous and disintegrated, whereby their subsequent reduction is facilitated.

Calamine was formerly roasted in kilns, but is now generally calcined in reverberating furnaces. Zincblende is occasionally submitted to a preliminary roasting in kilns, so as to utilise the sulphurous acid which is evolved; but in all cases it requires to be ground, and the calcination completed in reverberatory calciners, similar to those used in copper-smelting.

Reduction.—The roasted ore is mixed with half its weight of powdered charcoal, coke, or anthracite, and introduced into crucibles or retorts of peculiar construction. In Silesia, whence the greater part of the zinc used in the arts is obtained, the mixture of zinc-oxide and charcoal or coke is heated in muffles 3 feet long and 1½ foot high, six of which (three side by side) are laid in one furnace. The evolved mixture of carbonic oxide gas and zinc-vapour passes from the upper and fore part of the muffles, through a knee-shaped channel, horizontal in the nearer and directed downwards in the farther part, and the zinc condenses therein, and drops down from its lower aperture. Part of the zinc-vapour, and likewise some cadmium-vapour, escapes uncondensed, together with the carbonic oxide gas, and burns in the air, producing the substance called *Silesian Zinc-flowers*. In Liège, the reduction is performed in earthernware tubes, laid side by side. The zinc, as it condenses in the fore part of these tubes, is scraped out from time to time in the liquid state. In England, a number of cast-iron pots are arranged in a circle in one common furnace. Through the bottom of each of these pots there passes a tube, open at both ends. The vessels are filled with the mixture to such a height as not to stop up the upper end of the tube, then closed with a well-fitting cover, and heated. The zinc drops down from the part of the tube which descends from the bottom of the crucible. This process is called *Destillatio per descensum.*—At Goslar, in the Harz, zinc is obtained as a secondary product in the smelting of lead-ores. The zinc-vapours condense in the upper half of the furnace, and run down from the shaft upon a slanting stone called the *zinc-stool*. The zinc thus obtained is melted in iron pots, and poured out on tables.*

Purification.—Commercial zinc contains small quantities of lead and iron, together with minute quantities of tin and cadmium, and occasionally traces of arsenic and copper. Carbon is also mentioned amongst its impurities; but Eliot and Storer did not find it in either of the thirteen specimens which they examined, though traces of sulphur were always present. The best mode of obtaining pure zinc is to pass sulphuretted hydrogen through a strong and somewhat acid solution of zinc-sulphate, filtering from any precipitate that may be formed, and, after boiling the solution to expel the sulphuretted hydrogen, precipitating the zinc as carbonate by addition of sodium-carbonate. The carbonate, after being washed, is redissolved in pure sulphuric acid, and the zinc is reduced by electrolysis; or the dried carbonate may be converted into oxide by ignition, and the oxide distilled in a porcelain retort, with charcoal prepared from loaf-sugar.

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* For details and figures, see *Ure's Dictionary of Arts, &c.* iii. 1072, and Miller's *Elements of Chemistry*, 3rd ed., part ii. p. 540.

Properties.—Zinc is a white metal, with a shade of blue, capable of being polished, and then assuming a bright metallic lustre. It is usually brittle, and its fracture exhibits a crystalline structure. But zinc, if pure, may be hammered into thin leaves, at the usual temperature; and commercial zinc, which is impure and brittle at a low temperature, acquires the same malleability between 100° and 150°: it may then be laminated; and the metal is now consumed, in the form of sheet-zinc, for a variety of useful purposes. At 210° it again becomes brittle, and may be reduced to powder in a mortar of that temperature. The density of cast zinc is 6·862, but it may be increased by forging to 7·21. It melts at 412° (Daniell), and boils at 1040° (Deville and Troost). At a red heat, zinc rises in vapour, and takes fire in the air, burning with a white flame like that of phosphorus; the white oxide produced is carried up mechanically in the air, although itself a fixed substance. Laminated zinc is a valuable substance, from its slight disposition to undergo oxidation. When exposed to air, or placed in water, its surface becomes covered with a grey film of suboxide, which does not increase; this film is better calculated to resist both the mechanical and chemical effects of other bodies than the metal itself, and preserves it. Ordinary zinc dissolves with facility in dilute *hydrochloric*, *sulphuric* and other *hydrated acids*, by substitution for hydrogen. Pure zinc dissolves very slowly in the same acids, unless it is in contact with platinum, copper, or any other less positive metal, with which it can form a galvanic circuit. Ordinary zinc dissolves more quickly than the pure metal, because the lead contained in it is precipitated in the metallic state, and acts as an electronegative element to the zinc (see Electricity, ii. 420). In consequence of this electrolytic action, zinc, in contact with iron or copper in a saline solution, protects the other metal from oxidation.—*Galvanised iron* consists of iron having its surface coated with zinc, which, in like manner, protects it from oxidation in air and water. Zinc precipitates silver, copper, mercury, and most of the basylous metals, less oxidable than itself, from their acid solutions.

Zinc dissolves also in aqueous alkalis, with evolution of hydrogen, forming a zincate of the alkali-metal: *e.g.*, $Zn + 2KHO = K^2Zn''O^2 + H^2$. In this case, also, the solution of the zinc is accelerated by contact with less oxidable metals, as platinum, iron, &c.

Zinc reduces many metallic *oxides* (chromic oxide, for example) when melted with them. Nearly all *chlorides* and *fluorides* are reduced when heated with zinc-vapour in an atmosphere of hydrogen (Poumarède, J. pr. Chem. lxxiii. 496). At a very high temperature, zinc reduces *carbonic anhydride*, forming *oxide of zinc*; at a somewhat lower temperature, on the contrary, charcoal reduces oxide of zinc (p. 1067).

Zinc is a diatomic metal, and forms, for the most part, but one class of compounds: $ZnCl^2$, ZnO, $Zn(NO^3)^2$, $ZnSO^4$, &c. A lower and a higher oxide are known, but they are not of very definite character.

ZINC, ALLOYS OF. Zinc unites with nearly all other metals, forming alloys which are mostly hard, and in some cases brittle. They may be prepared by directly fusing the two metals together; if, however, the heat be allowed to rise too high, the zinc will be volatilised. Most of the zinc-alloys have been already described in connection with other metals.

Zinc does not form an alloy with bismuth; on mixing the two metals in the melted state, the mass separates into two layers—one consisting of zinc containing 2·4 per cent. bismuth, the other of bismuth containing from 8·6 to 14·3 per cent. zinc. (Matthiessen and v. Bose.)

Tin unites readily with zinc by fusion, forming alloys which are harder than tin, but softer than zinc; they are also less malleable than tin. An alloy of 11 pts. tin to 1 pt. zinc beaten out into leaf, forms spurious silver-leaf. According to Rudberg, the alloy $ZnSn^6$ (1 pt. tin to 10¾ pts. zinc) solidifies completely at 204°; but all the other alloys separate on cooling from a state of fusion into two portions, the one consisting of $ZnSn^6$, not solidifying till cooled to 204°, while the remainder, consisting of an alloy containing a larger proportion of one or the other metal, solidifies at a higher temperature: thus—

	$Sn^{12}Zn$.	Sn^6Zn.	Sn^4Zn.	Sn^3Zn.	Sn^2Zn.	$SnZn$.
Variable point . . .	210°	. .	230°	250°	280°	320°.
Fixed point . . .	204°	204°	204°	204°	204°	204°.

Respecting the alloys of zinc, tin, and lead, see Lead (iii. 538).

Alloys of zinc, tin, and copper constitute many varieties of bronze, tombac, &c. Alloys containing smaller proportions of zinc are used, on account of their hardness, to form the journals and other parts of machines. (See Copper, Alloys of, ii. 461.)

According to Calvert and Johnson, the alloys $ZnCu^{10}Sn$ and $ZnCu^{18}Sn$ are definite chemical compounds, inasmuch as they are scarcely attacked by nitric acid of specific gravity 1·1, or by concentrated hydrochloric acid, and not at all by sulphuric acid, of specific gravity 1·6. Both these alloys, on account of their hardness, are well adapted to form parts of machinery.

Some bronzes contain lead as well as copper, tin, and zinc: thus, *British bell-metal* consists of 5·6 pts. zinc, 10·1 tin, 80·0 copper, and 4·3 lead; and the *biddery-ware* of India, of 3 pts. of an alloy of copper, tin, and lead (16 pts. copper to 4 pts. lead and 2 pts. tin), to 16 pts. zinc. (Williams.)

An *amalgam* of zinc and tin is used for coating the rubbers of electrical machines.

ZINC, BROMIDE OF. $ZnBr^2$.—This compound is formed directly by igniting zinc in bromine-vapour. A solution of zinc or zinc-oxide in aqueous hydrobromic acid solidifies, at a certain degree of concentration, to an indistinctly crystalline, very deliquescent mass of the hydrated bromide mixed with a certain quantity of oxide, which, when heated, yields a sublimate of zinc-bromide in white needles of specific gravity 3·643, and a residue of zinc-oxide. According to Kremers (Pogg. Ann. ciii. 57; civ. 133; cviii. 115), solutions of zinc-bromide of different strengths exhibit, at 19·5°, the specific gravities shown in the following table:—

Quantity of $ZnBr^2$ in 100 pts. water .	20·6	42·6	76·0	91·4	111·2	150·3	213·0	318·3
Specific gravity at 19·5° .	1·1715	1·3770	1·5276	1·6101	1·7082	1·8797	2·1027	2·3914

A solution of zinc-bromide in ammonia yields, by evaporation, colourless octahedrons of zinc-ammonium-bromide, $(N^2H^6Zn'')Br^2$, which are decomposed by heat and by water. (Rammelsberg.)

By the simultaneous action of zinc and bromine on anhydrous ether, there is formed, together with bromide of carbon, an unstable compound of ether and zinc-bromide, which fumes in the air and dissolves in water. (Nicklès, Compt. rend. lii. 870.)

Zinc-bromide unites with the bromides of alkali-metals, forming double salts, exactly like the corresponding chlorine-compounds. The ammonium-salt has a specific gravity of 2·628. (Bödecker.)

ZINC, CHLORIDE OF. $ZnCl^2$. *Butter of Zinc. Butyrum Zinci.*—Very thin zinc-foil takes fire at ordinary temperatures in chlorine-gas. Zinc-chloride is formed in the wet way by dissolving zinc or zinc-oxide in hydrochloric acid, or by decomposing certain metallic chlorides in solution with zinc or a zinc-salt: thus, when a solution containing equivalent quantities of zinc-sulphate and sodium-chloride is cooled, zinco-sodic sulphate crystallises out at + 10°; but at 0°, pure sodic sulphate separates, while zinc-chloride remains in solution.—Anhydrous zinc-chloride may be prepared by distilling 1 pt. of zinc-filings with 2 pts. of mercuric chloride, or 1 pt. zinc-oxide with 2 pts. sal-ammoniac, or by distilling the residue left on evaporating the aqueous solution; also by distilling a mixture of dry zinc-sulphate and calcium-chloride.

Zinc-chloride is a whitish-grey translucent substance, soft like wax, and of specific gravity 2·753; it has a burning taste and emetic action; melts easily, and distils or sublimes in white needles at a red heat; deliquesces quickly on exposure to the air, and dissolves easily in water and in alcohol.

The aqueous solution evaporated to a syrup, with addition of a little hydrochloric acid, deposits a hydrated salt, $ZnCl^2.H^2O$, in small deliquescent octahedrons. The specific gravities of solutions of various strengths are, according to Kremers, as follows:

Quantity of $ZnCl^2$ in 100 pts. water .	16·7	38·8	56·3	92·4
Specific gravity at 19·5° . . .	1·331	1·2714	1·3677	1·5336

A saturated alcoholic solution of zinc-chloride deposits an alcoholate, $ZnCl^2.C^2H^6O$, in small crystals. (Graham.)

Anhydrous zinc-chloride is a powerful dehydrating agent, acting upon organic bodies like oil of vitriol; thus it chars wood, converts alcohol into ether, and has been recommended by Kraft and Mottay (Compt. rend. xlviii. 410), instead of sulphuric acid, for the preparation of fatty acids from glycerides. Even the concentrated aqueous solution destroys vegetable fibre, and cannot therefore be filtered through paper; according to Persoz, it dissolves silk.

A dilute aqueous solution of zinc-chloride is much used, under the name of *Burnett's Disinfecting Fluid*, as an antiseptic, and for preserving wood and vegetable fibre against decay. The concentrated solution is used in the laboratory as a bath for heating substances to a constant temperature. The dry chloride, obtained by evaporation, is used in surgery as a caustic.

Zinc-chloride combines easily with *ammonia*, with *chlorides of alkali-metal*, and with *zinc-oxide*, forming several oxychlorides.

a. With Ammonia.—When a hot concentrated solution of zinc-chloride is treated with gaseous or aqueous ammonia, till the resulting precipitate redissolves, the solution, on cooling, deposits the compound $4NH^3.ZnCl^2.H^2O$, in shining scales or laminæ, which, when heated to 150°, give off water and ammonia, and leave zinc ammonium-

chloride, $2NH^3.ZnCl^2 = (N^2H^6Zn'')Cl^2$, in the form of
pound separates also, in shining rhombic crystals, fro
solution of zinc-chloride—sometimes immediately, so
of the diammoniacal compound. Both the precedin
heated, give off ammonia, and leave a clear liquid, wh
imperfectly crystalline mass of the compound $ZnCl^2$.N
at a red heat, and is resolved by water into zinc ammo
an oxychloride, $ZnCl^2.6ZnO.6H^2O$. (Kane.)

β. With Alkaline Chlorides.—Zinc-chloride uni
ammonium-chloride.—The salt $2NH^4Cl.ZnCl^2$ is produ
at a gentle heat, in aqueous sal-ammoniac, or 1 pt. zin
in strong hydrochloric acid; it crystallises on evapora
in large laminæ containing 1 at. water of crystallisatio
9·28 pts. boiling water. The dry salt is resolved by he
chloride. Rammelsberg (Pogg. Ann. xciv. 507) obt
anhydrous rhombic crystals, by evaporating a mixed
ammonium-chloride.—Marignac (Ann. Min. [5], xi
solution containing about 2 at. sal-ammoniac to 1 at.
$3NH^4Cl.ZnCl^2$, the mother-liquor of which deposited rh
salt, $2NH^4Cl.ZnCl^2$.—The salt $NH^4Cl.ZnCl^2$ crystallise
ammoniac and 2 pts. zinc-chloride, in easily soluble rh
water (Hautz, Ann. Ch. Pharm. lxvi. 287). A conce
chloride of zinc and ammonium is used to remove the fi
metals, such as zinc, iron, or copper, which are to be un

Zinco-potassic chloride, $2KCl.ZnCl^2$, forms rhombi
2·297, isomorphous with the similarly constituted amm
more deliquescent than the latter (Marignac).—*Zin*
$3H^2O$, crystallises in small very deliquescent needles
system. (Marignac.)

γ. With Zinc-oxide.—When aqueous zinc-chloride i
the chlorine escapes as hydrochloric acid, and the residu
basic chloride of zinc, only partly soluble in water.—
or $ZnCl^2.3ZnO.4H^2O$, is obtained by boiling a strong
zinc-oxide, or by precipitating the solution with an ins
and digesting the precipitate with the liquid: it forms
a soft, white powder, and gives off half its water at 10
$6ZnO.10H^2O$, is formed by the action of water on
$NH^3.ZnCl^2$ (*vid. sup.*), or by precipitating zinc-chlori
sufficient to redissolve part of the precipitate. It is a w
and giving off half its combined water at 100°.—$Zn^{10}Cl^2$
remains as a white insoluble powder, when a solution
to a syrup, and then treated with water. The same
combination with $14H^2O$, on mixing a solution of zi
potash just sufficient to produce an alkaline reaction.

Persoz (Compt. rend. lv. 310) uses a basic solution
boiling a solution of the neutral chloride of about 1·70
excess of zinc-oxide), for dissolving silk, and separatin
fibres.

When zinc-oxide is boiled with a strong solution of
tions, a plastic mass is obtained, which, after a while,
used for taking casts. A cement, prepared by addi
glass-powder to 50 pts. of a solution of zinc-chloride of
1 pt. of borax dissolved in the smallest possible quan
Paris for stopping teeth, and for making artificial teeth
cl. 78). An oxychloride of zinc, prepared by a similar
paint for wood, paper, stone, or metal. It dries quickl
(Sorel.)

ZINC, CYANIDE OF. See CYANIDES (ii. 274).

ZINC, DETECTION AND ESTIMATION
tions.—All zinc-compounds, when heated with *sodium*
give an incrustation of zinc-oxide, which is yellow while
ing; it is not volatile in the outer flame. With *borax*,
either flame a bead, which is yellowish while hot, white
zinc-salt is present. If the colourless bead or the
with a dilute solution of *cobalt-nitrate*, and strongly he
green colour is produced.

2. *Reactions in Solution.*—Zinc-salts are colourless, and form colourless solutions.—*Sulphydric acid* gives, with neutral solutions of zinc-salts, a white precipitate of zinc-sulphide, which does not contain all the zinc; in solutions containing a sufficient quantity of free hydrochloric or sulphuric acid, no precipitate is formed; but from acetate of zinc, or any zinc-salt mixed with acetate of sodium, zinc is completely precipitated by sulphydric acid, even if a large quantity of free acetic acid is present. Sulphide of zinc is insoluble in caustic alkalis.—*Sulphide of ammonium* precipitates zinc-salts completely.—*Cyanide of potassium* throws down white cyanide of zinc, soluble in excess, and reprecipitated by sulphide of ammonium.—*Ferrocyanide of potassium* forms a white precipitate, insoluble in hydrochloric acid.—*Oxalic acid* and *phosphate of sodium* precipitate white oxalate and phosphate of zinc, soluble in acids and alkalis; the phosphate is not precipitated in presence of sal-ammoniac and ammonia.—*Fixed alkaline carbonates* precipitate a white basic carbonate, insoluble in excess, soluble in alkalis; chloride of ammonium hinders this precipitation in the cold.—*Potash, ammonia*, and *carbonate of ammonium* form white precipitates soluble in excess, reprecipitated on diluting with water and on boiling; soluble also in chloride of ammonium. Sulphydric acid precipitates zinc-sulphide from these solutions.

Zinc in solution is distinguished from all other metals by the precipitation of its white sulphide by sulphide of ammonium, in a solution containing excess of caustic alkali.

3. *Estimation and Separation.*—Zinc is precipitated from its solutions by *carbonate of sodium*, which, when added in excess, and boiled with the solution, throws down carbonate of zinc. It is best, however, to pour the zinc-solution into the hot solution of the alkaline carbonate, because, in that case, we may be sure of not forming a basic salt. If the zinc-solution contains ammoniacal salts, it must be boiled with a quantity of carbonate of sodium sufficient to decompose those salts, then evaporated to dryness, the residue treated with a large quantity of water to dissolve out the soluble salts, and the carbonate of zinc collected on a filter, and well washed with hot water. The evaporation should be conducted as quickly as possible. The carbonate of zinc, when dried and ignited, yields oxide of zinc containing 80·26 per cent. of the metal.

In separating zinc from other metals, it is often necessary to precipitate by *sulphide of ammonium*. If the solution is acid, it must be previously neutralised by ammonia. The precipitate must not be thrown on the filter immediately, but left to settle down completely, after which the clear liquid must first be passed through the filter, and then the precipitate thrown on it. If this precaution be neglected, the sulphide of zinc will stop up the pores of the filter. The precipitate is washed with water containing a little sulphide of ammonium; then dissolved in hydrochloric acid; the solution boiled to drive off the sulphydric acid; and the zinc precipitated by carbonate of sodium as above.

Zinc is separated from all the non-metallic elements, and from the metals of alkalis and alkaline-earths (barium, strontium, and calcium), by *sulphide of ammonium*. In the case of the alkaline earths, however, great care must be taken to prevent the ammoniacal liquid from absorbing carbonic acid from the air, as that would occasion a precipitation of the earth-metal in the form of carbonate. For this purpose, the filtration must be effected as quickly as possible, and the liquid well protected from the air. The separation of zinc from barium may also be effected by *sulphuric acid*, and from calcium by *oxalate of ammonium*.

From magnesium, zinc may be separated by *sulphide of ammonium*, a sufficient quantity of chloride of ammonium being previously added, to prevent the precipitation of the magnesia; or the separation may be effected by converting the zinc and magnesium into acetates, and precipitating the zinc as sulphide by *sulphydric acid*.

The separation of zinc from aluminium, glucinum, and chromium (in the form of chromic oxide) may also be effected by converting the bases into acetates, and precipitating the zinc with *sulphydric acid*, or by dissolving in potash, and precipitating the zinc with sulphydric acid; but the first method is to be preferred. Chromium, in the form of chromic acid, is separated from zinc, as from other metals, by fusion with an *alkaline carbonate* (i. 145).

The conversion into acetates, and precipitation by sulphydric acid, likewise serves to separate zinc from zirconium, yttrium, thorinum, and manganese. The separation from manganese may also be effected by converting the two metals into chlorides, passing *chlorine-gas* through the solution to convert the manganese into dioxide, and completing the precipitation of the latter with *carbonate of barium*.

From iron, zinc may be separated by *ammonia*, or (better) by *succinate of ammonium* (iii. 386). The iron (in the state of ferric oxide) may also be precipitated by *carbonate of calcium* or *barium*.

Uranium, as uranic oxide, may be separated from zinc by this latter mode of precipitation.

For the methods of separating zinc from cobalt (i. 1047; iv. 39).

From molybdenum, tungsten, and vanadium, insolubility of its sulphide in sulphide of ammonium. it from titanium, see p. 839.—From thallium, zinc the thallium with *iodide of potassium* (p. 749).

From arsenic, antimony, copper, and all other soluble in acids, zinc is separated by precipitating thos in solutions containing excess of mineral acid.

4. *Atomic Weight of Zinc.*—Gay-Lussac (Mé dising zinc with nitric acid, and by measuring the quant zinc dissolves in dilute acids, concluded that 100 pts. pts. oxygen: whence Zn = 64·56.—Berzelius (Gilb. An first method, nearly the same number.—Jacquelain by the decomposition of the nitrate and sulphate of zinc ing with the number 66·24; and Favre's experime composition of zinc-oxalate, and on the quantity of hy solves in hydrochloric acid, give the number 66·0 for th sequently (in 1844), A. Erdmann (Ann. Ch. Pharm. of zinc, mixed it with pure charcoal obtained from suga of hydrogen; he then oxidised the metal with nitric aci by ignition. The atomic weight of zinc, calculated from thus conducted, is 65·04. The same number was obtain of zinc-lactate.

ZINC, FLUORIDE OF. ZnF^2.—Zinc dissolves and the solution, when evaporated, deposits the hydrat shining, rhombic octahedrons, exhibiting the combinati Zinc-fluoride dissolves slowly but completely in water, mo fluoric, hydrochloric, or nitric acid, or of ammonia. W it dissolves oxide of zinc.

Zinc-fluoride forms double salts with the fluorides —The *aluminium-salt*, $ZnF^2.Al^2F^6$, forms long colourle $2KF.ZnF^2$, colourless crystalline grains.

ZINC, HYDRATE OF. See ZINC, OXIDE OF (p.

ZINC, IODIDE OF. ZnI^2.—Finely-divided zin forming an easily fusible compound, which sublimes 4·696. The same compound separates in regular octahe evaporating a solution obtained by digesting iodine wit the colour of the iodine disappears.

Zinc-iodide is very deliquescent, and dissolves easily i of the solution varies with its strength, in the manner (Kremers):—

Quantity of ZnI^2 in 100 pts. water .	21·5	30·0	46·4	74·4
Specific gravity at 19·5°	1·1715	1·2340	1·3486	1·5121

Zinc-iodide is decomposed when heated in contact wit and zinc-oxide produced.

The aqueous solution dissolves zinc in contact with th deposits an oxyiodide on cooling (Müller, J. pr. solution, digested with iodine, forms a brown liquid zinc.

Dry zinc-iodide absorbs 27 per cent. (nearly 6 at.) loose white powder, soluble in acids but decomposed b iodide in aqueous ammonia deposits, by spontaneous ev prisms of the compound $4NH^3.ZnI^2$, which is also deco

Zinc-iodide unites with iodides of alkali-metals, double salts, which may be crystallised by evaporation $2NH^4I.ZnI^2$, $KI.ZnI^2$, $NaI.ZnI^2.\frac{3}{2}H^2O$, and $BaI^2.2ZnI$

ZINC, NITRIDE OF. This compound is form electrolysis of water containing sal-ammoniac, when t zinc and the negative pole of platinum.

ZINC, OXIDES OF. Only one oxide of zinc is protoxide. The grey film, which forms on the surface of regarded by Berzelius as a suboxide; but it is proba oxide with metallic zinc. Thénard also states that a gelatinous peroxide is produced by the action of hydric peroxide on hydrated zinc-oxide.

Zinc-oxide, ZnO.—This oxide occurs native, contaminated with manganese-oxides, as zincite or red zinc-ore, and combined with the sesquioxides of manganese and iron, as franklinite, both of which minerals are found at Sterling Hill, Sussex County, New Jersey—the former in hexagonal, the latter in monometric forms. It is formed by the combustion of zinc in the air, and by ignition of zinc-salts containing volatile acids; frequently also in the smelting of metallic ores containing zinc, and is occasionally deposited in furnace-flues in six-sided prisms. Crystallised zinc-oxide is also produced by heating zinc-chloride in a current of aqueous vapour.

The ordinary amorphous oxide is obtained, as a fine flocculent powder, by burning zinc in contact with the air. When zinc is thrown, by small quantities at a time, into a capacious earthen crucible previously heated to whiteness, it burns with a bright bluish-white flame, and deposits large flakes of the oxide mixed with small particles of the metal mechanically carried over: from these the oxide may be freed by levigation with water, the heavier metallic particles then subsiding, and leaving the pure oxide in suspension. This oxide is much used as a pigment, called zinc-white, and is manufactured for this purpose by distilling zinc from clay-retorts into chambers through which a current of air is kept up. The volatilised metal burns at the high temperature to which it is exposed under these circumstances, and the oxide is deposited in a series of condensing-chambers. The white pigment thus obtained is permanent, not being blackened, like white lead, by exposure to sulphuretted hydrogen; it is also much less poisonous than white lead. An impure oxide, sold under the name of tutty, is obtained from the flues of furnaces in which brass is melted.—For pharmaceutical purposes, zinc-oxide is prepared by igniting the precipitated hydrate or carbonate.

Zinc-oxide, when crystallised, forms transparent, yellowish, six-sided prisms of about 6·0 specific gravity. The ordinary oxide is a white amorphous powder, of about 5·6 specific gravity. It is insoluble in water. When heated it assumes a lemon-yellow colour, but becomes white again on cooling. It is very refractory in the fire, but is said to volatilise at the strongest white heat. It is easily reduced by charcoal, less easily by hydrogen or carbonic oxide. When heated with sulphur, it forms zinc-sulphide and sulphurous anhydride; with chlorine, at a red heat, it yields zinc-chloride, which distils over, and free oxygen.

Zinc-oxide is a strong base, dissolving completely in acids, and forming the zinc-salts. It also acts as a base towards oxides of the form M^2O^3; thus with alumina it forms gahnite, $ZnO.Al^2O^3$.—A solution of zinc-oxide in potash deposits, on addition of chromic hydrate, a green compound containing $ZnO.Cr^2O^3$ (Chancel).—Ebelmen (Ann. Ch. Phys. [3], xxxiii. 34) obtained such compounds (spinels) crystallised, by heating the component oxides with boric oxide for a long time in a pottery-furnace, till the boric oxide was volatilised.—The compound $ZnO.Cr^2O^3$ formed small blackish-green octahedrons, of specific gravity 5·309; $ZnO.Fe^2O^3$, microscopic, shining, black octahedrons, of specific gravity 5·132; $ZnO.Al^2O^3$ (gahnite), colourless octahedrons, harder than quartz, and having a specific gravity of 4·58.

Hydrated Zinc-oxide, or *Zinc-hydrate.*—Anhydrous zinc-oxide does not unite directly with water. Zinc-salts treated with ammonia yield a white gelatinous zinc-hydrate, soluble in excess of potash or ammonia. A crystallised monohydrate, $ZnO.H^2O = Zn''H^2O^2$, is obtained by immersing zinc in aqueous ammonia in contact with iron (Runge; Schindler), or with lead or copper (Nicklès). Hydrogen is then evolved, and after some time zinc-hydrate is deposited on the zinc in rhombic prisms, of specific gravity 2·677 (see also Cornu, Bull. Soc. Chim. 1863, p. 64).—A dihydrate, $ZnO.2H^2O = Zn''H^4O^3$, is deposited from a saturated solution of zinc-oxide in soda-ley, left to itself for a long time in a closed vessel. It forms colourless regular octahedrons, having a strong adamantine lustre, retaining their lustre and transparency after washing with water and drying over chloride of calcium, but becoming white when hot water is poured upon them. Zinc-hydrate dissolves readily in dilute acids, caustic alkalis, and carbonate of ammonium. It easily gives off its water when heated.

ZINC, OXYCHLORIDE OF. See ZINC, CHLORIDE OF (p. 1070).

ZINC, OXYSULPHIDE OF. See ZINC, SULPHIDES OF (p. 1074).

ZINC, PEROXIDE OF. (See p. 1070.)

ZINC, PHOSPHIDES OF. (Hoos, Ann. Ch. Pharm. c. 101.)—The compound Zn^3P^2 was obtained by strongly igniting 2 at. zinc-oxide with 1 at. phosphoric anhydride and 7 at. charcoal, and collected in the neck of the retort as a brittle sublimate, which had a dark steel-grey colour, and dissolved in hydrochloric acid, with evolution of non-spontaneously inflammable phosphoretted hydrogen.—Zinc-oxide, ignited in phosphorus-vapour, forms a black crystalline mass, together with a red phosphide of zinc. The black mass boiled with hydrochloric acid, left a grey crystalline powder, probably consisting of ZnP^2.

ZINC, SELENIDE OF. Formed by passing selenium-vapour over red-hot zinc. It is a lemon-yellow pulverulent body, from which nitric acid dissolves the zinc, and at first separates the selenium, but on prolonged action dissolves it as selenious acid. (Berzelius.)

ZINC, SELENIOCYANATE OF. See SELENIOCYANATES (p. 220).

ZINC, SILICOFLUORIDE OF. See SILICOFLUORIDES (p. 273).

ZINC, SUBOXIDE OF. (See p. 1072.)

ZINC, SULPHIDES OF. Of these compounds, the best known is that which corresponds to the oxide. According to Schiff, there is also a pentasulphide, ZnS^5.

The *protosulphide*, ZnS, occurs native as blende, in monometric forms, viz. ∞O (*fig.* 178, CRYSTALLOGRAPHY, ii. 124); $\pm \frac{O}{2}$ (*fig.* 189); the same with the two tetrahedrons equally developed, forming a regular octahedron (*fig.* 172); and $\frac{O}{2} \cdot \infty O$ (*fig.* 203); also twins like *fig.* 319 (ii. 160), and others; cleavage perfect parallel to ∞O. The mineral likewise occurs in botryoïdal and other imitative shapes, and massive, compact. Hardness = 3·5 to 4. Specific gravity = 3·9 to 4·2. Transparent to translucent. Lustre resinous to adamantine. Colour brown, yellow, black, red, green, white, or yellow when pure. Streak white to reddish-brown. Fracture conchoïdal. Brittle.

Analyses.—*a.* Franklin, New Jersey: colourless, transparent (Henry).*—*b.* Claussthal: crystallised, black (Kuhlemann).—*c.* Raibl, Carinthia: scaly (Kersten).—*d.* Przibram, Bohemia: radiate (Löwe).—*e.* Eaton, New Hampshire (Jackson).—. Shelburne, New Hampshire (Jackson).—*g.* Christiania: black-brown, radiate (Scheerer).—*h.* Marmato, near Popayan, South America: *marmatite*: black (Boussingault).—*i.* Bottino, near Serravezza, Tuscany: massive (Bechi):

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Sulphur	32·22	33·04	32·10	33·75	32·22	32·6	33·73	33·73	33·65
Zinc	67·46	65·39	64·22	61·62	63·62	52·0	53·17	51·95	48·11
Cadmium	. . .	0·79	trace	1·78	0·60	3·2			
Iron	. . .	1·18	1·32	2·20	3·10	11·3	12·53	14·32	16·23
Copper	. . .	0·13	0·72	99·35	100·54	99·1	99·43	100·00	97·99
Antimony	. . .	0·63	0·80 †						
	99·68	101·16	99·16						

Blende occurs in both crystalline and sedimentary rocks, and is usually associated with galena; also with heavy spar, copper-pyrites, spathic iron, and frequently in silver-mines. Derbyshire, Cumberland, and Cornwall afford the black varieties called *black jack*; also Transylvania, Hungary, and the Harz. Sala in Sweden, Ratieborzitz in Bohemia, and many Saxon localities, afford splendid black and brown crystals.

Zinc-sulphide cannot be formed by fusing sulphur and zinc together, because the sulphur volatilises before combination can take place; but it is produced, with detonation, when zinc-filings are heated with cinnabar or potassium-sulphide. It is likewise obtained by heating zinc-oxide with sulphur alone, or with sulphur and charcoal; by heating zinc-oxide or the hydrated sulphide in a stream of sulphydric acid gas; and, finally, by reducing zinc-sulphate with sulphur or charcoal. When prepared by either of these methods, it is a white or yellowish powder, of specific gravity 3·92: it melts at a very high temperature, and volatilises only at a white heat.

Crystallised zinc-sulphide is easily oxidised by fusion with nitre; slowly, but completely, when heated in contact with the air: acids decompose it slowly, with evolution of sulphydric acid. The amorphous sulphide is decomposed by atmospheric oxidation, or by acids, more quickly than the crystallised sulphide.

The *hydrated sulphide*, $ZnS.H^2O$, obtained by precipitation (p. 1071), and dried at 100°, is a white powder, which, when more strongly heated, gives off its water and turns yellowish. It oxidises quickly on exposure to the air, and dissolves easily in dilute mineral acids, slightly in a large excess of acetic acid. (Wackenroder.)

Oxysulphides.—Zinc-sulphide, when dried in the air, generally contains a small quantity of oxide. Oxysulphides of zinc are found in furnace-flues. Kersten (Schw. J. lvii. 186) found one in a furnace at Freiberg, having the composition $ZnO.4ZnS$; the zinc-oxide was not dissolved out of it by acetic acid. The same compound occurs, as voltzite or voltzine, in implanted spherical globules with galena, blende, &c., at Rosières in Puy-de-Dôme, and in the Elias mine, near Joachimsthal in Bohemia.

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* For references, see Rammelsberg's *Mineralchemie*, p. 48.

† Lead.

The compound Zn^2OS, or $ZnO.ZnS$, is formed, according to Arfvedson (Pogg. Ann. l. 59), when dry zinc-sulphate is heated to redness in a stream of hydrogen.

Pentasulphide of Zinc, ZnS^5, is formed, according to Schiff (Ann. Ch. Pharm. cxv. 74), when a neutral zinc-salt is precipitated by pentasulphide of potassium. The precipitate is white, but acquires a straw-yellow colour when pressed and dried. When heated in a close vessel, it is resolved into the protosulphide and free sulphur. It dissolves in acids, with evolution of sulphydric acid gas, and separation of sulphur.

ZINC, TELLURIDE OF. Zinc and tellurium unite when fused together, with great evolution of heat. The product is grey, crystalline, difficult to fuse, insoluble in dilute sulphuric or concentrated hydrochloric acid. (Berzelius.)

ZINCACETAMIDE, $C^4H^8Zn''N^2O^2$, is a white powder formed by the action of acetamide on zincethyl.

ZINCAMIDE, N^2H^4Zn'', is produced by the action of ammonia on zincethyl (p. 1076).

ZINCAMYL, or **ZINCAMYLIDE.** See ZINC-RADICLES, ORGANIC.

ZINC-ASH. The impure grey oxide, or suboxide of zinc, formed when zinc is heated in contact with the air.

ZINCAZURITE. This name is given by Breithaupt (Berg- u. Hüttenm.-Zeit. vi. 101), to a blue mineral occurring in the veins of Baranco Jaroso, in the Sierra Almagrera in Spain, and containing, according to Plattner and Richter, cupric oxide, zinc-oxide, sulphuric acid, and a little water.

ZINCBLENDE. Native sulphide of zinc (p. 1074).

ZINC-BLOOM, or **ZINCONISE.** A native hydrocarbonate of zinc. (See CARBONATES, i. 798).

ZINC-BUTTER. *Butyrum Zinci.*—Syn. with ZINC-CHLORIDE (p. 1069).

ZINC-DINITROETHYLATE. (See p. 1077.)

ZINCETHYL, or **ZINCETHIDE.** See ZINC-RADICLES, ORGANIC (p. 1076).

ZINC-ETHYLAMYLATE. (See p. 1077.)

ZINC-FAHLORE, or copper-blende from near Freiberg, is a tennantite (p. 720), having the iron partly replaced by zinc.

ZINC-FLOWERS. *Flores Zinci.*—Zinc-oxide produced by combustion of the metal (p. 1073).

ZINC-GLASS. }
ZINC-GRAMMATITE. } Syn. with SILICEOUS CALAMINE (i. 713).

ZINCITE, or *Red Zinc Ore.* Native oxide of zinc containing manganese (p. 1074).

ZINCKENITE. Syn. with ZINKENITE (p. 1079).

ZINC-METHYL, or **ZINC-METHIDE.** See ZINC-RADICLES, ORGANIC (p. 1078).

ZINCONISE. Syn. with ZINC-BLOOM.

ZINC-PHENYLAMIDE. A product of the action of zincethyl on aniline.

ZINCPHYLLITE. Syn. with HOPEITE (iii. 106).

ZINC-RADICLES, ORGANIC. Zinc unites with alcohol-radicles (methyl, ethyl, and amyl), forming compounds analogous in composition to zinc-chloride, or zinc-oxide, and represented by the general formula $Zn''R^2$. They are saturated compounds, not capable of uniting directly with oxygen, chlorine, or other elements, and are therefore not radicles in the proper sense of the word, like cacodyl, stibtrimethyl, stannethyl, &c. They are produced by heating zinc with the iodides of the alcohol-radicles in sealed tubes, and by the action of zinc on the mercury-compounds of the same radicles. The first method is best adapted for the preparation of zincethyl, the second for obtaining the methyl- and amyl-compounds. (See ORGANO-METALLIC BODIES, iv. 219).

Zincamyl, or **Zincamylide,** $Zn(C^5H^{11})^2$.—Prepared by heating zinc with mercuric amylide

$$Hg(C^5H^{11})^2 + Zn^2 = Zn(C^5H^{11})^2 + ZnHg.$$

It is a colourless, transparent, mobile liquid, of specific gravity 1·022 at 0°, boiling at 220°. Vapour-density, obs. = 6·95; calc. (2 vols.) = 6·87. It decomposes gradually at 240°, yielding amylene and amylic hydride. In contact with the air it fumes, but does not take fire. When dropped into oxygen-gas, it burns with a dazzling white

ame and slight explosion. Its reactions with oxygen
isely analogous to those of zincethyl (iv. 225).

Zincethyl, or **Zincethide,** $Zn(C^2H^5)^2$.—This body
1849, is prepared by heating zinc, in a closed vessel, w
ether (iv. 219). For preparation on the small scale, th
glass tubes, and heated in an oil- or air-bath; for large
trived by Frankland, and described in the article BATH
(Ann. Ch. Pharm. cxviii. 22; cxxi. 105), dehydrates equ
iodide with phosphoric anhydride, and heats the mixtu
with carbonic anhydride at a pressure about one-fourth g
air,—with granulated zinc previously strongly etched
thoroughly dried.—Rieth and Beilstein (*ibid.* cxx
alloy of 4 pts. zinc and 1 pt. sodium with ethylic iod
bonic anhydride. Chapman adopts a very similar pr
start the reaction (*Laboratory*, i. 195). Alexeyeff a
lxiii. 171) heat 100 grms. ethylic iodide, in a simil
zinc-sodium, and 70 to 80 grms. zinc-cuttings.—Zince
heating granulated zinc with about half its volume
retort in the water-bath for 36 hours (Frankland an
3).—Zincethyl is also produced by the action of zinc
(Wanklyn):

$$Zn + Hg + 2NaC^2H^5 = Zn(C^2H$$

Zincethyl is a transparent, colourless, strongly refra
odour rather agreeable than otherwise. Specific gravit
solidify at −22°, boils at 118°, and distils without d
obs. = 4·259; calc. (2 vols.) = 4·262. In contact wi
takes fire, burning with a bright-green-edged flame, and
zinc-oxide. It is also rapidly decomposed by water, wi
and zinc-hydrate:

$$Zn(C^2H^5)^2 + 2H^2O = 2(C^2H^5.H)$$

The reactions of zincethyl with oxygen, the halo
oxide, phosphorous chloride, oxalic ether, ammonia, &c
under ORGANO-METALLIC BODIES (iv. 225, 226). We
covered since that article was written:—

With *chloride of acetyl* and its homologues, zincethyl
alcohols, according to the manner in which the react
chloride of acetyl is added by drops to 1 at. zinceth
to 0° and filled with carbonic anhydride, a strong action
be immediately treated with water, a ketone boiling a
composition of acetyl-ethyl, $C^4H^8O = C^2H^3O.C^2H$
seems to take place between 2 at. chloride of acetyl and

$$2C^2H^3OCl + Zn(C^2H^5)^2 = ZnCl^2 +$$

But if the liquid be left to itself for some days, it bec
warmed and treated with water, a large quantity of co
the liquid, acidulated with hydrochloric acid and disti
homologous with pseudobutylic alcohol—viz., methyl
$\left.\begin{matrix}[C(CH^3)(C^2H^5)^2]'\\ H\end{matrix}\right\}O.$ (See the corresponding reaction

Chloride of butyryl, C^4H^7OCl, yields with zince
butyryl-ethyl, $C^4H^7O.C^2H^5$, or propyl-diet
$\left.\begin{matrix}[C(C^3H^7)(C^2H^5)^2]\\ H\end{matrix}\right\}O.$ (Freund, Ann. Ch. Pharm. cxvi
Buttlerow, Bull. Soc. Chim. 1866, i. 17; Jahresb. 18
benzoyl, zincethyl yields benzoyl-ethyl, $C^7H^5O.C^2H$
Ann. Ch. Pharm. cxix. 165).—With *phenylsulphurous c*
chloride and phenylsulphurous hydride. (Kalle.)

2. When zincethyl is heated in sealed tubes with *all*
tion takes place, resulting in the formation of ethy
iodide, allyl, C^6H^{10}, amylene, C^5H^{10}, amylic hydride,
(Wurtz, Ann. Ch. Pharm. cxxiii. 202).—Zincethyl, h
to 120°, yields a liquid which has an alliaceous odour,
80°. (Olevinsky, Jahresb. 1861, p. 664.)

3. *Tetrachloride of carbon* acts strongly on zincethyl,
and propylene (Rieth and Beilstein, Ann. Ch.

$$2CCl^4 + 3Zn(C^2H^5)^2 = 2C^2H^5Cl + 2C^2H$$

4. *Chloroform* acts less strongly, producing amylene, and probably ethylic hydride, together with small quantities of ethylene and propylene (Reith and Beilstein).—With *bromoform* a strong action takes place, resulting in the formation of propylene and ethylic bromide (Alexeyeff and Beilstein, Compt. rend. lviii. 172):

$$CHBr^3 + Zn(C^2H^5)^2 = C^3H^6 + C^2H^5Br + ZnBr^2.$$

Iodoform likewise acts strongly on zincethyl, apparently combining directly with it.

5. *Chloriodoform*, added by drops to zincethyl, forms chloride and iodide of zinc, together with ethylene, ethyl (tetrylic hydride), and free hydrogen (Borodine, Ann. Ch. Pharm. cxxvi. 239):

$$2CHCl^2I + 3Zn(C^2H^5)^2 = 7C^2H^4 + 2H^2 + 2ZnCl^2 + ZnI^2.$$
$$2CHCl^2I + 3Zn(C^2H^5)^2 = 3C^2H^4 + 2C^4H^{10} + 2ZnCl^2 + ZnI^2.$$

6. *Dichloride of carbon* does not act on zincethyl under the ordinary atmospheric pressure.—*Trichloride of carbon* is reduced to dichloride, with formation of ethylic chloride and zinc-chloride.

7. Zincethyl is not attacked by *chloride of triethylstibine*, $Sb(C^2H^5)^3Cl^2$, even at the boiling heat; but with the *iodide* it appears to form antimonic pentethide, $Sb(C^2H^5)^5$, which is then decomposed according to the equation:

$$Sb(C^2H^5)^5 = Sb(C^2H^5)^3 + C^2H^4 + C^2H^6.$$

(Buckton, Chem. Soc. Qu. J. xiii. 125.)

8. Pure zincethyl attacks *amylic nitrite* with great violence, bursting out into flame when placed in contact with it. But if the zincethyl be considerably diluted with ether, and added to an excess of amylic nitrite, nitric oxide is evolved, and a honey-like mass is formed, which, on treatment with water, yields amylic alcohol, ethylic alcohol, ethylic hydride, and probably ethyl-amylic ether, thus:

$$2NO(C^5H^{11})O + Zn(C^2H^5)^2 = \underbrace{\left.\begin{matrix}ZnC^2H^5\\ C^5H^{11}\end{matrix}\right\}O \cdot \left.\begin{matrix}C^2H^5\\ C^5H^{11}\end{matrix}\right\}O}_{\text{Honey-like mass.}} + 2NO.$$

$$\underset{\text{Zincethyl-amylate.}}{Zn(C^2H^5)(C^5H^{11}O)} + 2H^2O = \underset{\text{Zinc-hydrate.}}{Zn(HO)^2} + \underset{\text{Ethyl-hydride.}}{C^2H^6} + \underset{\text{Amyl-alcohol.}}{C^5H^{12}O.}$$

The ethylic alcohol is probably formed by the action of water on the ethyl-amyl-ether, $(C^2H^5)(C^5H^{11})O$, contained in the honey-like substance.—When amylic nitrite is dropped into excess of zincethyl diluted with five or six times its weight of ether no gas is evolved; but, nevertheless, the action appears to be the same as that just described, excepting that the nitric oxide produced is immediately absorbed by the excess of zincethyl, forming the compound of zinc-dinitroethylate with zincethyl described under DINITROETHYLIC ACID (iv. 61).—When only a small quantity of ether is mixed with the zincethyl, triethylamine is formed, as shown by the equation:

$$N'''\left\{\begin{matrix}O''\\ OC^5H^{11}\end{matrix}\right. + 3\ \frac{Zn}{2}\ C^2H^5) = \frac{ZnO}{\frac{Zn}{2}OC^5H^{11}} + N(C^2H^5)^3.$$

(Chapman and Smith, Chem. Soc. J. vol. xxi. 1868.)

9. When *amylic nitrate* is mixed with undiluted zincethyl in an atmosphere of carbonic anhydride, no change takes place at first; but if the mixture be exposed for an instant to the air, it explodes with a vivid flash of light and sharp report, and with extreme violence if heated to about 40°. Dilution with ether renders the reaction manageable, and if the mixture be then heated to 110°, complete decomposition takes place. (Chapman and Smith.)

Respecting the action of zincethyl on other compound ethers, see ORGANO-METALLIC BODIES (iv. 226), and OXALIC ETHERS (iv. 272).

10. With *monochlorinated ethylic oxide*, zincethyl yields a liquid having the composition $C^6H^{13}ClO$, apparently $C^4H^8Cl(C^2H^5)O$, or monochlorethylic oxide having one atom of the hydrogen replaced by ethyl. (Lieben and Bauer, Ann. Ch. Pharm. cxxiii. 130.)

11. Zincethyl, gently heated for some hours with *aldehyde*, forms a compound having nearly the composition of acetal.—On *valeral* and *œnanthol* it appears to exert a dehydrating action (Rieth and Beilstein).—*Bitter-almond oil* is strongly attacked by zincethyl.—*Acetone* acts strongly on zincethyl, especially when heated, forming an oil having, in general, the properties and nearly the composition of phorone, $C^9H^{14}O$.

12. An ethereal solution of zincethyl, added in excess to *amylene disulphochloride* (i. 209), separates into two layers; and on adding water, and drying and distilling the oil which floats on the surface, the compound $C^{10}H^{20}S^2Cl^2$ passes over between 240° and 250°. (Guthrie, Ann. Ch. Pharm. cxxi. 108.)

13. *Carbonic disulphide* unites with zincethyl, formin
as a brown shining mass, which gives off sulphide of a
(Grabowski, Ann. Ch. Pharm. cxxxviii. 165; Jahresb

Zinc-methyl, or **Zinc-methide,** $Zn(CH^3)^2$.—This
Frankland in 1849, is formed by heating methylic iodid
150°; but the method is not advantageous, since a la
formed, and escapes forcibly on opening the tube, carr
The preparation is greatly facilitated by mixing the met
its bulk of ether, and heating to 100° in the copper app
of zincethyl (p. 1076). On rectifying the product, a liq
consisting of zinc-methyl, mixed or combined with et
$Zn(CH^3)^2$ to 1 at. $(C^2H^5)^2O$.—When methylic ether, con
stead of ethylic ether to dilute the methylic iodide, a li
obtained, consisting nearly of 2 at. $Zn(CH^3)^2$ to 1 at. (
nor the methylic ether can be separated from the zinc-m
Pharm. cxi. 62). Pure zinc-methyl may, however, be
zinc-methyl and ethylic ether just mentioned, by enclosi
and methylic iodide, heating the mixture to 100°, and d
tillate contains a larger proportion of zinc-methyl than
repeating the process a certain number of times, nearly
(Wanklyn, Chem. Soc. Qu. J. xiii. 124). According
however (Chem. Soc. J. xvii. 30), the best mode of prep
heat finely-granulated zinc with half its volume of merc
to 120° for 24 hours, and distil off the product.

Zinc-methyl is a colourless liquid, of specific gravity
stantly at 46° (Frankland and Duppa). Vapour-densit
3·296. The vapour bears a temperature of 200° witho
it decomposes, with separation of zinc and gaseous hyd

Zinc-methyl takes fire immediately in contact with th
greenish-blue flame; in oxygen-gas it burns with expl
vapour mixed with combustible gases render them spon

In its chemical reactions, zinc-methyl exhibits for the
zincethyl; in some cases, however, differences are obser
dride (iii. 1003; iv. 225).—*Water* decomposes zinc-met
gas (methylic hydride), and separation of zinc-hydrate.

With *chloride of lead*, zinc-methyl forms plumbic d
chloride, with separation of lead. (Buttlerow, Bull.

An ethereal solution of zinc-methyl added to *iodide*
ethide, $Sn^{iv}(C^2H^5)^2I^2$, forms iodide of zinc and stannic eth

With *mercuric chlorethide*, zinc-methyl appears to form
ethylomethide, $Hg(C^2H^5)(CH^3)$, which however is resolv
mercuric ethide and mercuric methide.

Antimonic di-iodotrimethide, $Sb(CH^3)^3I^2$, acts strong
zinc-methyl, forming antimonious methide (stibmethyl),
tamethide, $Sb(CH^3)^5$, which cannot be completely s
(Buckton, Chem. Soc. Qu. J. xiii. 115.)

With *chloride of acetyl* and its homologues, zinc-met
ing acetones or tertiary alcohols, according as the prod
with water immediately, or after some time only. In
the product formed in the first case is ordinary acetone,
but when the liquid formed by gradually adding 1 at. cl
methyl, is left to itself for a few hours, it solidifies to lar
pound $C^6H^{15}Zn^2OCl = C^2H^3OCl \cdot 2Zn(CH^3)^2$. The
take place in the manner represented by the equation
$\left.\begin{matrix}[C(CH^3)^2]' \\ (CH^3Zn)'\end{matrix}\right\}O + (CH^3Zn)'Cl$, inasmuch as the crystals
resolved into marsh-gas, zinc-hydrate, zinc-chloride, an
methyl-carbinol):

$$\left.\begin{matrix}C(CH^3)^3 \\ CH^3Zn\end{matrix}\right\}O + CH^3ZnCl + 4H^2O = \left.\begin{matrix}C(CH^3)^3 \\ H\end{matrix}\right\}O$$

With *chloride of butyryl*, in like manner, zinc-meth
thyl, $C^4H^7O.CH^3$, or tertiary octylic alcohol (propyl
$\left.\begin{matrix}C(C^3H^7)(C^2H^5)^2 \\ H\end{matrix}\right\}O$. (Buttlerow, Zeitschr. Ch. Pharm
1864, p. 496; Bull. Soc. Chim. 1866, i. 17; Jahresb. 186

With *chloride of carbonyl* (phosgene), zinc-methyl form which, when treated with water, yields a distillate, apparently consisting of the compounds $C^4H^{10}O$ and C^3H^8O.

Ethylic chlorocarbonate (i. 916) is strongly attacked by zinc-methyl at a gentle heat, yielding zinc-chloride, carbonic anhydride, ethylene, and marsh-gas.—With *methylic chlorocarbonate*, the action is similar, but less energetic; the substances must be heated together in a sealed tube, and even then the decomposition is not complete. (Butlerow, Bull. Soc. Chim. 1863, p. 588.)

ZINC-SPAR. Syn. with CALAMINE (i. 713).

ZINC-SPINEL. Syn. with GAHNITE (ii. 757).

ZINCUM. Syn. with ZINC (p. 1067).

ZINC-VITRIOL. Syn. with ZINC-SULPHATE. (See SULPHATES, p. 617).

ZINC-VITRITE. Syn. with SILICEOUS CALAMINE (i. 714).

ZINC-WHITE. Zinc-oxide used as a pigment (p. 1073).

ZINGIBER. See GINGER (ii. 838).

ZINKENITE. $Pb''Sb^2.S^4 = Pb''S.Sb^2S^3$. *Zinckenite. Rhombohedral Dystomeglance.*—A sulphantimonite of lead, occurring in the antimony-mine at Wolfsberg in the Harz, in trimetric crystals, usually in twins, as hexagonal prisms terminated by low hexagonal pyramids; lateral faces longitudinally striated; sometimes columnar, fibrous, or massive. Cleavage not distinct. Hardness = 3 to 3·5. Specific gravity = 5·30 to 5·35. Lustre metallic. Colour and streak steel-grey. Opaque. Fracture slightly uneven. (H. Rose, Pogg. Ann. viii. 99.—Brun Kerl, Berg. u. hüttenm. Zeit. 1853, No. 2.—Dana, ii. 74.)

ZIPPEITE. A basic uranic sulphate found at Joachimsthal in Bohemia.

ZIRCON. ZIRCONITE. $ZrSiO^4 = ZrO^2.SiO^2$. *Jargon. Hyacinth.*—A mineral occurring in quadratic crystals, the predominant faces of which are P, ∞P, ∞P∞. Length of principal axis = 0·6405. Angle P : P (terminal) = 123° 19′; P : P (lateral) = 84° 20′. Cleavage imperfect parallel to ∞P. Occurs also in irregular forms and in grains. Hardness = 7·5. Specific gravity = 4·0—4·75. Lustre more or less adamantine. Colour red, brown, yellow, grey, or white. Streak uncoloured. Transparent to subtranslucent. Fracture conchoïdal and brilliant. Before the blowpipe it loses colour, but is infusible alone, also with sodium-carbonate and microcosmic salt. With borax it melts with difficulty to a diaphanous glass, which, with more of the flux, is opaque.

Pure zircon contains 33·2 per cent. silica and 66·8 zirconia; some specimens contain small quantities of lime and ferric oxide.

The name *hyacinth* includes the bright-coloured varieties of zircon, which are sometimes large enough to be valuable as gems; the greyish or brownish kinds are called *zirconite*. A variety from Ceylon, which is colourless or has only a smoky tinge, and is therefore sold for inferior diamonds, is sometimes called *jargon*.

Hyacinth occurs in the sand and alluvial deposits of certain rivers in Ceylon; at Expailly, near La Puy, in France; at Ohlapian in Transylvania, Pfitsch in the Tyrol, Bilin in Bohemia, Lebnitz in Saxony, occasionally in volcanic tufa in Auvergne; also in Greenland; in the zircon-syenite of Frederichsvärn in Norway; near Brevig, sometimes called *Erdmannite*; at Miask, in the Urals; in the iron-mines of Arendal; also in Scotland, at Scalpay in Harris, and in the granite of Criffel in Kirckudbrightshire; on Vesuvius, with ryacolite, in white and blue octahedrons; at Santa Rosa, in New Granada, in small colourless crystals; and at several localities in North Carolina, New York, New Jersey, Pennsylvania, California, and Canada (Dana, ii. 196).—Breithaupt's *Ostranite*, supposed to be from Frederichsvärn, is a greyish-brown zircon.

Zircon is one of the most unalterable of minerals, but is sometimes found in a hydrated state, and is probably acted upon by alkaline waters, which take up part of the silica: *calypolite* (i. 723), *malacone* (iii. 784), *œrstedtite* (iv. 179), and *tachyaphaltite* (v. 654), appear to be zircons thus altered.

ZIRCONATES. See ZIRCONIUM, OXIDE OF (p. 1084).

ZIRCONIA. Oxide of Zirconium (p. 1083).

ZIRCONIC ACID. Zirconia in combination with bases (p. 1084).

ZIRCONITE. See ZIRCON.

ZIRCONIUM. *Symbol*, Zr; *Atomic Weight*, 89·6.—An element belonging to the group of earth-metals, and apparently forming a link between aluminium and silicium. Its oxide, zirconia, was first obtained from zircon, and recognised as a peculiar substance by Klaproth, in 1789; it has since been found in eudialyte, polymignite, œrstedtite, fergusonite, and catapleïite. Aschynite, formerly supposed to contain zirconium, has been shown, by recent experiments of Hermann (Bull. Soc. Chim. 1866, ii. 386) to be free from it.

Metallic zirconium is capable, like silicium, of existing in three states—amorphous, crystalline, and graphitoïdal.—*Amorphous zirconium* was obtained by Berzelius (in 1824), in the same manner as amorphous silicium and boron—namely, by heating a mixture of potassio-zirconic fluoride with potassium, digesting the fused mass with water containing a little hydrochloric acid, and washing the metal which remains undissolved with sal-ammoniac solution, and then with alcohol. It may also be prepared by passing chloride of zirconium in vapour over sodium contained in a red-hot porcelain tube, or by heating sodio-zirconic chloride in a crucible with sodium or magnesium (Troost, Compt. rend. lxi. 109; Bull. Soc. Chim. 1866, i. 213). Zirconium thus obtained is an amorphous powder, compressible under the burnisher into thin, faintly lustrous, graphitic laminæ. In the unignited state it diffuses itself through water in extremely fine particles, which pass through a filter; but it settles down slowly on standing, more quickly on addition of acids or salts. It does not conduct electricity, is not altered by ignition in hydrogen; but if it be then brought in contact with the air, after cooling, the metal becomes heated to redness, in consequence of the heat evolved by the absorption of the air. When heated in the air, it takes fire at a heat considerably below redness, and burns with a bright light, forming zirconia. It is but little attacked by the ordinary acids, or by nitromuriatic acid; but hydrofluoric acid dissolves it readily, with evolution of hydrogen, and a mixture of hydrofluoric and nitric acids attacks it very energetically.

Crystalline zirconium is prepared by heating 1 pt. of potassio-zirconic fluoride with 1½ pt. aluminium in a plumbago crucible, to the melting-point of iron. When the crucible has cooled, the surface of the aluminium is found to be covered with foliated crystalline laminæ, consisting of nearly pure zirconium, which may be separated by dissolving out the aluminium with hydrochloric acid. Crystalline zirconium thus obtained is very hard, and resembles antimony in colour, lustre, and brittleness. It crystallises in broad laminæ, apparently derived from a monoclinic prism. Specific gravity = 4·15. It is less fusible than silicium, and burns only at the temperature of the oxyhydrogen-blowpipe. It takes fire at a red heat in chlorine-gas, and decomposes hydrochloric acid gas at the same temperature. It is but slowly attacked by sulphuric, nitric, or hydrochloric acid, even when heated; hot nitromuriatic acid attacks it rapidly; hydrofluoric acid also dissolves it readily, even in the cold. (Troost.)

Graphitoïdal zirconium appears to be formed only under peculiar circumstances. Troost, in attempting to decompose zirconate of sodium with iron, obtained zirconium in small very light scales, of a steel-grey colour.

Zirconium is a tetratomic element, like silicium, its oxide being ZrO^2, the chloride $ZrCl^4$, &c. It forms but one class of compounds with chlorous elements. The oxide is capable of acting both as a base and as an acid.

ZIRCONIUM, BROMIDE OF. A solution of zirconium-hydrate in hydrobromic acid leaves, on evaporation, a hydrated bromide in crystalline grains, which are resolved by heat into zirconia and hydrobromic acid. (Berzelius.)

ZIRCONIUM, CHLORIDE OF. $ZrCl^4$.—This compound is formed, with incandescence, when zirconium is heated in chlorine-gas; also by heating a mixture of zircon or zirconia with charcoal, in a stream of dry chlorine, in which case it collects in the cooler part of the apparatus as a white sublimate. Its vapour-density, as determined by Deville and Troost (Ann. Ch. Pharm. cv. 213), is 8·15; by calculation from the formula, $ZrCl^4$, for a two-volume condensation, it is 8·0. The chloride dissolves easily, and with rise of temperature, in water.

A *hydrated chloride* is obtained, by evaporating a solution of zirconic hydrate in hydrochloric acid, in colourless silky needles, having an astringent taste, easily soluble in water and in alcohol, sparingly soluble in concentrated hydrochloric acid. (Berzelius.)

These crystals become opaque at 50°, giving off part of their water and half their hydrochloric acid, and leaving a basic chloride or oxychloride containing $ZrCl^4.ZrO^2.18H^2O$, or $ZrOCl^2.9H^2O$. The same compound is obtained, in stellate groups of white silky prisms, on evaporating the aqueous solution of zirconium-chloride. These crystals, when heated, become white and turbid, and are converted into the anhydrous dioxychloride $ZrCl^4.2ZrO^2$. (Hermann.)

ZIRCONIUM, DETECTION AND ESTIMATION OF. The reactions of zirconium-salts with alkalis, alkaline carbonates, and ammonium-sulphide are very similar to those of thorinum, yttrium, and the metals of the cerium-group. The precipitate formed by *caustic alkalis* and *ammonia* contains alkali, and is insoluble in excess of the reagent (distinction from aluminium and glucinum), also in sal-ammoniac. The precipitate formed by *alkaline carbonates* and *bicarbonates* redissolves in excess of the reagent.—A characteristic reaction is afforded by a hot concentrated solution of *potassic sulphate*, which, when added to a hot solution of a zirconium-salt, throws down the zirconium as basic potassio-zirconic sulphate, insoluble in water, and nearly insoluble even in a large quantity of hydrochloric acid.—Zirconium is precipitated from its solution by boiling with *hyposulphite of sodium*, a character by which it may be distinguished from yttrium and the cerium-metals. From cerium and from didymium it is further distinguished by not giving any coloured reactions before the blowpipe. The methods of distinguishing it from thorinum have already been given (p. 786).

For the *quantitative estimation* of zirconium in solutions containing only volatile acids, it is sufficient to evaporate to dryness, and ignite the residue, whereby zirconia is obtained, containing 73·68 per cent. of the metal. Zirconium may also be precipitated from such solutions by ammonia as a basic salt, which also leaves pure zirconia when ignited.

From yttrium, the cerium-metals, and iron, zirconium may be separated by boiling the solution with *hyposulphite of sodium*, which precipitates the zirconium alone as hyposulphite. This precipitate when ignited leaves pure zirconia. To effect complete separation from the cerium-metals by this method, the solution must be dilute. For separating zirconium from iron (as ferric salt) by the same method, Chancel (Ann. Ch. Pharm. cviii. 237) and Stromeyer (*ibid.* cxiii. 127) recommend that the dilute solution, after being nearly saturated with sodic carbonate, be mixed cold with sodic hyposulphite till it is completely decolorised; if the liquid be then boiled as long as sulphurous anhydride continues to be evolved, the zirconium is completely precipitated as oxide, while the whole of the iron remains dissolved as ferrous salt. The separation of zirconium from these metals may also be effected by treating the boiling solution with *sulphate of potassium*, and adding a drop or two of ammonia, whereby the zirconium is precipitated, and the other metals remain dissolved. (H. Rose.)

Precipitation with *hyposulphite of sodium* serves also to separate zirconium from phosphoric and boric acids.

From thorinum, zirconium is separated by *oxalate of ammonium*, which, when added in excess, precipitates the thorinum as oxalate, and holds the zirconium in solution.

From titanium, tantalum, and niobium, zirconium may be separated by precipitation with *sulphate of potassium*.

Atomic Weight of Zirconium.—Berzelius (Pogg. Ann. iv. 124; viii. 186) found that sulphate of zirconium contains 75·583 pts. zirconia to 100 pts. sulphuric anhydride (mean of eight experiments). Hence the atomic weight of zirconium is 44·7, 67·0, or 89·4, according as zirconia is regarded as ZrO, Zr^2O^3, or ZrO^2. Hermann (J. pr. Chem. xxxi. 77), by the analysis of chloride of zirconium, obtained very nearly the same numerical results. Now the vapour-density of the chloride calculated from the formula $ZrCl^4$, with $Zr = 89·4$, for a two-volume condensation, agrees very nearly with the experimental number obtained by Deville and Troost (p. 1080); and Marignac has shown that double-salts of zirconium-fluoride are isomorphous with those of silicium-fluoride. Hence zirconium is regarded as a tetratomic element, having the atomic weight 89·4.

ZIRCONIUM, FLUORIDE OF. ZrF^4.—Strongly ignited zirconia dissolves with difficulty in hydrofluoric acid: the hydrate dissolves abundantly. *Anhydrous zirconium-fluoride* is formed by heating zirconia with twice its weight of ammonium-hydrogen-fluoride (ii. 670), till the fluoride of ammonium is completely driven off. It dissolves readily in water acidulated with hydrofluoric acid; and when its solution containing excess of hydrofluoric acid is evaporated, *hydrated zirconium-fluoride*, $ZrF^4.3H^2O$, separates out in small, shining, triclinic crystals, mostly of the tabular form. They give off hydrofluoric acid as well as water when heated, and if the heat be continued for some time (even below redness), pure zirconia remains behind. Fluoride of zirconium dissolves without decomposition in dilute hydrofluoric acid, but when it is dissolved in pure water, a basic fluoride or oxyfluoride separates out. (Marignac.)

Fluozirconates.—Zirconium-fluoride unites with many other metallic fluorides, forming double salts isomorphous with the corresponding fluosilicates (silicofluorides, p. 271), fluostannates (p. 813), and fluotitanates (p. 840). The ratio of the fluorine of the zirconium-fluoride to that of the basic metallic fluoride in these salts is as 1 : 1; 1 : $1\frac{1}{3}$; 1 : 2; and 1 : 4; the sodium-salt alone exhibiting the ratio 5 : 8. The general formulæ of the fluozirconates are, therefore, $4MF.ZrF^4$, $3MF.ZrF^4$, $2MF.ZrF^4$, and $MF.ZrF^4$, the sodium-salt alone having the formula $5NaF.2ZrF^4$. The fluozirconates have been examined chiefly by **Marignac.** (Ann. Ch. Phys. [3], lx. 257; Ann. Ch. Pharm, cxv. 359; Jahresb. 1860, p. 136, *et seq.*)

The fluozirconates are mostly soluble in water, and crystallise well. They are prepared by mixing the component fluorides, or by dissolving a metallic oxide or carbonate in a mixture of zirconium-fluoride and hydrofluoric acid.

The fluozirconates of barium, strontium, and calcium are insoluble in water; consequently the solutions of fluozirconates are precipitated by salts of these metals. When a solution of zirconium-fluoride containing free hydrofluoric acid is mixed with carbonate of barium, carbonic anhydride is expelled, and a precipitate is formed, consisting of a mixture of insoluble barium-zirconium fluoride with insoluble barium-fluoride; similarly with the carbonates of strontium and calcium.

Many fluozirconates dissolve without decomposition in water, either hot or cold. Many are decomposed when their aqueous solutions are boiled, part of the basic metallic fluoride being deposited, and a fluozirconate containing $2MF.ZrF^4$ remaining in solution. Most fluozirconates, when heated in contact with moist air, give off all their fluorine as hydrofluoric acid, leaving a mixture of zirconia and the oxide of the other metal; when heated with a sufficient quantity of sulphuric acid, they yield a mixture of zirconium-sulphate with the sulphate of the other metal.

Fluozirconates of Ammonium.—The *diammonic salt*, $2(NH^4)F.ZrF^4$, forms rhombic crystals, isomorphous with the potassium-salt: they do not lose weight at 100°.—The *triammonic salt*, $3(NH^4)F.ZrF^4$, crystallises from a solution containing a large excess of ammonium-fluoride, in regular cubo-octahedrons.

Barium-salt.—A solution of the potassium-salt, mixed with chloride of barium, yields a white precipitate, consisting of $3Ba''F^2.2ZrF^4.2H^2O$, or perhaps a mixture of this salt with barium-fluoride.

Cadmium-salts.—The *dicadmic salt*, $2CdF^2.ZrF^4.6H^2O$, forms monoclinic crystals isomorphous with the manganese-salt, and having the angle $\infty P : \infty P = 79° 31'$; $+P : +P = 100° 30'$; $+2P : +2P = 75° 24'$; $oP : \infty P = 108° 29'$; $oP : \infty P\infty = 119° 43'$; the same crystals are obtained by recrystallisation from water. A solution containing excess of zirconium-fluoride deposits the salt $CdF^2.2ZrF^4.6H^2O$, in fan-shaped groups of laminar crystals.

Copper-salts.—The *tricupric salt*, $3CuF^2.2ZrF^4.16H^2O$, forms monoclinic crystals, and crystallises unaltered from solution in water; but a solution containing excess of zirconium-fluoride deposits, besides the larger crystals of this salt, light-blue crusts of zirconium-fluoride contaminated with adhering copper-salt.

Lead-salt.—When a solution of zirconium-fluoride in hydrofluoric acid is saturated with carbonate of lead, fluozirconate of lead partly remains undissolved and partly dissolves, the solution yielding on evaporation a granulo-crystalline salt, which is quickly decomposed by water, especially in presence of hydrofluoric acid, with separation of lead-fluoride.

Magnesium-fluozirconate, $MgF^2.ZrF^4$, forms small shining crystals with curved faces, isomorphous with the manganese-salt. It is only sparingly soluble in water, but crystallises by slow evaporation, often in twins. By prolonged heating in contact with the air, it is converted into magnesia and fluoride of zirconium.

Manganese-salts.—The *monomanganous salt*, $MnF^2.ZnF^4.5H^2O$, forms monoclinic crystals, isomorphous with the magnesium-salt, but the faces are flat and more numerous: the crystals cleave imperfectly parallel to oP. By prolonged heating in the air it turns black, and is converted into manganic peroxide and zirconium-fluoride.—A solution containing excess of zirconium-fluoride yields rose-coloured monoclinic crystals of the *dimanganous salt*, $2MnF^2.ZrF^4.6H^2O$, which dissolves in water without alteration, and is not decomposed even on heating the solution; but when hot water is poured upon the crystals, fluoride of manganese separates, and the solution yields by evaporation crystals of the preceding salt.

Nickel-salts.—The *normal salt*, $NiF^2.ZrF^4.6H^2O$, forms hexagonal prisms, terminated by faces of a rhombohedron of 127° 10', and cleaving parallel to the prismatic faces.—The salt $2NiF^2.ZrF^4.12H^2O$, produced in presence of an excess of nickel-fluoride, forms monoclinic crystals of a fine emerald-green colour, but mostly indistinct: they dissolve without decomposition in water, but the solution, when boiled for some time, becomes turbid from separation of nickel-fluoride.

Fluozirconate of Nickel and Potassium, $NiF^2.2KF.2ZrF^4.8H^2O$, separates in small but regular monoclinic crystals, on mixing the solutions of the component fluozirconates. It is slightly soluble in water, does not lose water at 100°, but at a higher temperature gives off water, together with hydrofluoric acid.

Potassium-salts.—The *dipotassic salt*, $2KF.ZrF^4$, may be prepared by igniting zircon with 2 or 3 pts. by weight of acid potassium-fluoride, boiling the resulting mixture of fluosilicate and fluozirconate of potassium with water containing a little hydrofluoric acid, and filtering. The potassium-fluozirconate then separates on cooling, in anhydrous rhombic crystals terminated by six-sided pyramids. It dissolves in 128 pts. of water at 2°, in 71 pts. at 15°, in 59 pts. at 19°, and in 4 pts. at 100°. The crystals when heated to redness form a doughy mass, which, on exposure to moist air, gradually gives off all its fluorine as hydrofluoric acid. From dilute solutions the salt is obtained in larger crystals.—The *monopotassic salt*, $KF.ZrF^4.H^2O$, separates from a solution containing a large excess of zirconium-fluoride, in ill-defined monoclinic crystals, which give off their water at 100°, and hydrofluoric acid at a higher temperature. When recrystallised from water they yield the preceding salt.—The *tripotassic salt*, $3KF.ZrF^4$, crystallises from a solution containing an excess of potassium-fluoride, in very small but well-defined regular octahedrons, or cubo-octahedrons, which decrepitate when heated, but do not contain any water of crystallisation. They dissolve in water, and the hot saturated solution deposits the dipotassic salt on cooling.

Sodium-salt, $5NaF.2ZrF^4$.—This salt is always formed, in whatever proportion the component fluozirconates may be mixed. It forms small, mostly indistinct, monoclinic crystals, soluble in 258 pts. water at 18°, and in about 60 pts. of boiling water. On account of this slight solubility, the salt may be obtained by precipitating the more soluble fluozirconates with chloride of sodium. The dry crystals do not decompose at a red heat.

Zinc-salt, $ZnF^2.ZrF^4.6H^2O$.—This salt, isomorphous with fluosilicate and fluostannate of zinc, crystallises in rather large, regular, hexagonal prisms, terminated by rhombohedrons, and cleavable parallel to the faces of the hexagonal prism; they are very soluble in water. A solution containing excess of zinc-fluoride, deposits the salt $2ZnF^2.ZrF^4.12H^2O$, in monoclinic crystals, isomorphous with the corresponding nickel-salt; they dissolve completely in cold water, but the solution when boiled deposits fluoride of zinc.

ZIRCONIUM, NITRIDE OF. Zirconium strongly ignited in a rapid stream of ammonia-gas, yields a brown or black body containing nitrogen. Mallet (Sill. Am. J. xxviii. 346), by fusing amorphous zirconium with aluminium, in a cracked lime-crucible, obtained a dark-grey porous mass, which, when treated with hydrochloric acid, yielded microscopic cubes, having a golden lustre, not altered by nitromuriatic acid or aqueous alkalis, but giving off ammonia when fused with potassic hydrate.

ZIRCONIUM, OXIDE OF. *Zirconia.* ZrO^2.—This compound, the only known oxide of zirconium, is formed when the metal is heated to redness in contact with the air, or fused with the hydrates, carbonates, or hydrated borates of the alkali-metals. Zirconium is likewise oxidised, though slowly, by boiling with nitromuriatic or concentrated sulphuric acid.

Zirconia is prepared from zircon. The mineral is heated to redness and quenched in water, and the lumps (best those which are colourless, because free from iron) are finely pulverised and levigated. The levigated powder is mixed with four times its weight of sodium-carbonate, and very strongly heated in a platinum crucible. Henneberg and Wackenroder add a small quantity of nitre. Berzelius ignites the pulverised zircon with 3 pts. of sodium-carbonate, and lays small pieces of sodium-hydrate on the ignited mass from time to time, in such a manner that they may not touch the crucible. The pulverised zircon may also be decomposed by fusion with 3 or 4 pts. of sodium-hydrate in a silver crucible.

The disintegrated mass is supersaturated with hydrochloric acid; the liquid evaporated nearly to dryness to separate the silica; the residual mass digested with water; and the filtered solution treated with excess of ammonia, whereby zirconium is precipitated, generally mixed with ferric oxide.

The best method of separating the iron and obtaining pure zirconia, is to redissolve the precipitate in hydrochloric acid, and boil the solution with hyposulphite of sodium, whereby hyposulphite of zirconium is precipitated, while the whole of the iron remains in solution as ferrous salt. The washed precipitate is then boiled with hydrochloric acid as long as sulphurous acid continues to be evolved, and the solution of zirconium-chloride thus obtained is mixed with ammonia, whereby the zirconium is precipitated as a hydrate, which, when ignited, leaves anhydrous zirconia (Hermann). If the treatment with hyposulphite of sodium be conducted in the manner recommended by Chancel and Stromeyer (p. 1081), a precipitate of anhydrous zirconia is at once obtained.

The iron may also be precipitated by mixing the solution of zirconium-chloride containing iron with tartaric acid, then supersaturating with ammonia, and adding sulphide of ammonium. The iron is thereby precipitated as sulphide, and the filtered liquid, evaporated and ignited in contact with the air, leaves pure zirconia. [For other methods of separation, see Handw. d. Chem. ix. 1059; Gmelin's Handbook, iii. 340.]

Marignac decomposes zircon by ignition with hydrogen-ammonium-fluoride in the manner already described (p. 1081), heats the fluozirconate of potassium thereby obtained with strong sulphuric acid, and washes the strongly ignited residue with boiling water; pure zirconia then remains behind.

Zirconia, according to the mode in which it has been prepared, forms a white, tasteless, inodorous powder, or hard lumps of specific gravity 4·35 to 4·9, which scratch glass and give sparks with steel. Deville and Caron (Ann. Ch. Pharm. cviii. 55), by igniting fluoride of zirconium with borax in a closed crucible lined with charcoal, obtained zirconia in dendritic groups of small crystals resembling sal-ammoniac. When zirconia is fused with borax in a pottery-furnace, and the residue exhausted with hydrochloric acid, the zirconia remains in transparent, colourless, microscopic, quadratic prisms, isomorphous with tinstone and rutile, having a specific gravity of 5·71 to 5·72, and capable of polarising light. (Nordenskjöld, Pogg. Ann. cxiv. 612.)

When zirconia, prepared at the lowest possible temperature, is heated to commencing redness, it glows brightly, becomes dense, and is afterwards insoluble in ordinary acids, dissolves with difficulty even in hydrofluoric acid, and can be dissolved only by strong sulphuric acid, the finely pulverised earth being heated with a mixture of 2 pts. oil of vitriol and 1 pt. water. By ignition with charcoal in a stream of chlorine, zirconia is converted into chloride of zirconium.

Hydrate of Zirconia, or *Hydrate of Zirconium*, is precipitated from zirconium-salts by ammonia. When recently precipitated, it is a white bulky jelly, but shrinks in drying into a yellowish, translucent, gummy mass, having a conchoïdal fracture. The dry hydrate has, according to Berzelius, the composition, $Zr^{iv}H^2O^3 = ZrO^2.H^2O$; according to Hermann, the hydrate dried at 17°, is $Zr^{iv}H^4O^4 = ZrO^2.2H^2O$. (That obtained by Berzelius was probably dried at a higher temperature.) When ignited, it leaves pure zirconia. It dissolves in 5,000 pts. of water; the solution reddens turmeric-paper. (Brush.)

Zirconia acts both as a base and as an acid: hence called zirconic acid. The hydrate, when precipitated in the cold and washed with cold water, dissolves easily in acids: if precipitated from hot solution, or washed with hot water, it dissolves only in concentrated acids. The saturated solutions have an astringent sour taste, and redden litmus. [For their behaviour with reagents, see p. 1080.]

Zirconates.—Compounds of zirconia with the stronger bases are obtained by precipitating a zirconium-salt with potash or soda; also by igniting zirconia with an alkaline hydrate. Zirconate of potassium thus obtained, dissolves completely in water.

Sodium-salts.—*a. Disodic Zirconate*, $Na^2ZrO^3 = Na^2O.ZrO^2$, is easily obtained, by igniting zirconia with carbonate of sodium, as a crystalline mass which is gradually decomposed by water, with separation of amorphous zirconia.—*β.* When zirconia is heated to whiteness for a considerable time with excess of sodium-carbonate, 2 at. carbonic anhydride are evolved to 1 at. zirconia, and the salt $Na^4ZrO^4 = 2Na^2O.ZrO^2$ is produced. The fused mass treated with water, leaves small hexagonal laminæ of the following salt.—*γ.* An *acid salt*, $Na^2O.8ZrO^2.12H^2O$, is obtained as just described, or by fusing pulverised zircon with excess of sodic carbonate, and treating the mass with water containing hydrochloric acid. It forms hexagonal tables, sometimes aggregated in groups like those of clinochlore. (Hiortdahl, Ann. Ch. Pharm. cxxxvii. 24, 236; Jahresb. 1865, p. 185.)

Calcium-salt.—Zirconate of calcium is obtained by heating a mixture of silica and zirconia (in the proportions to form zircon) with excess of calcium-chloride to bright redness for five or six hours, and treating the product with hydrochloric acid. The zirconate then separates as a shining crystalline powder, together with flocculent silica and amorphous zirconia. (Hiortdahl.)

Zirconate of Magnesium is obtained by placing a mixture of silica and zirconia, together with excess of magnesium-chloride, in a platinum crucible, the bottom of which is covered with sal-ammoniac, heating the mixture quickly to whiteness, and continuing the heat for an hour. On treating the cooled mass with water containing hydrochloric acid, a crystalline powder is deposited, consisting of distinct octahedrons of periclase and prismatic crystals of magnesium-zirconate. (Hiortdahl.)

ZIRCONIUM, OXYCHLORIDES OF. See ZIRCONIUM, CHLORIDE OF (p. 1080).

ZIRCONIUM, SULPHIDE OF. Formed by heating zirconium with sulphur in a vacuum or in hydrogen-gas, the combination in the latter case being attended with slight incandescence. Dark cinnamon-brown powder, acquiring metallic lustre under the burnisher; not altered by water, dilute acids (even nitric acid), or aqueous alkalis; slowly dissolved by nitromuriatic acid; easily decomposed by hydrofluoric acid, with evolution of sulphydric acid. When fused with potash, it yields zirconia and sulphide of potassium.

Frémy, by igniting zirconia contained in a charcoal boat in a stream of carbonic disulphide vapour, obtained a compound (perhaps an oxysulphide) in steel-grey graphitoïdal scales, which yielded a yellow powder, were insoluble in water and in dilute acids, but were easily decomposed by nitric acid, with separation of sulphur.

ZIRCON-SYENITE. The zirconiferous syenite of South Norway.

ZOÏODIN. A name applied by Bonjean to a violet-coloured substance deposited, according to his observations, from the water which drips from baregin (i. 500), taken out of sulphurous springs.

ZOISITE. This name is sometimes applied to all lime-epidotes containing little or no iron (ii. 490); sometimes restricted to a mineral closely allied to epidote in composition and crystalline form, but differing somewhat in the cleavage. It occurs, according to Brooke and Miller, on the Sau Alp and at Sterzing in the Tyrol, at Fusch in Salzburg, at Baireuth and Conradsreuth near Hof in Bavaria, and in the Ural (Dana, ii. 211). Klaproth's analyses of two specimens from the Sau Alp gave:

SiO^2.	Al^2O^3.	Fe^2O^3.	CaO.	MnO.		
45	29	3	21	. .	=	98
44	32	2·5	20	trace	=	98·5

ZOMIDIN (from ζωμός, broth; diminutive ζωμίδιον).—A name applied by Berzelius to the portion of the aqueous extract of meat which is insoluble in alcohol, the soluble portion (about $\frac{4}{5}$ of the whole), being called *osmazome.*

ZOOCHEMICAL ANALYSIS. See ANALYSIS, ORGANIC (i. 250).

ZOOMELANIN. A name applied by Bogdanow (Compt. rend. xlvi. 780), to the black pigment of birds' feathers, probably identical with the melanin of the choroïd coating of the eye. The substance is slightly soluble in water, more soluble in potash and ammonia.

ZOONIC ACID. Berthollet's name for the impure acetic acid obtained by the dry distillation of animal substance.

ZOOSTEARIC ACID. Landerer's name for a fatty acid obtained from the bones of fossil mammalia, and crystallising from alcohol in laminæ. (Buchn. Repert. lxi. 90.)

ZOOTIC ACID. Syn. with HYDROCYANIC ACID (ii. 214).

ZOOTINE-SALT. Nitrate of sodium (iv. 105).

ZOOXANTHIN. The colouring-matter of the red feathers of *Calurus auriceps.* It may be completely extracted by repeated treatment with hot alcohol; and, on evaporating the solution at 60°—70°, there remains a dark-red powder, which, when thoroughly washed with water, leaves the zooxanthin, easily alterable by light. A similar pigment is said to be contained in the light-red fibres of *Calinga cœrulea.* (Bogdanow, Compt. rend. xlv. 688.)

ZORGITE. Native selenide of lead (clausthalite), containing copper or cobalt. (See LEAD, SELENIDES OF, iii. 557.)

ZOSTERA MARINA. This seaweed, which grows abundantly on nearly all seacoasts, leaves 23·3 per cent. ash, containing in 100 pts.: 3·9 pts. K^2SO^4, 4·4 KCl, 0·86 KI, 21·2 NaCl, 21·2 CaO, 5·6 $CaCO^3$, 2·1 $CaSO^4$, 9·8 $Ca^3P^2O^8$, 1·6 MgO, 25·1 SiO^2, 0·7 Al^2O^3, 1·9 Fe^2O^3, with traces of metallic bromide. (Baudrimont, J. Pharm. [3] xlii. 388.)

ZUMIC, or **ZYMIC ACID.** Names formerly applied to the acid (Braconnot's *nanceic acid*), produced in the fermentation of amylaceous substances: since known to consist of impure lactic acid.

ZURLERITE, or **ZURLITE.** Syn. with MELLILITE (iii. 869).

ZWIESELITE. Ferroso-manganous phosphato-fluoride, found in crystalline masses at Zwiesel, near Bodenmais in Bavaria. (See PHOSPHATES, iv. 571.)

ZYGADITE. A silicate of aluminium and lithium, occurring in the Katharina Neufang mine, at Andreasberg in the Harz. It forms twin-crystals, having the appearance of stilbite, slightly translucent, with reddish to yellowish-white colour, and vitreous lustre, inclining to nacreous on the cleavage-faces. Hardness = 6·3. Specific gravity = 2·511—2·512. (Breithaupt, Pogg. Ann. lxix. 441.)

ZYMIC ACID. Syn. with ZUMIC ACID.

ZYMIC INFUSORIA. *Zymiques*, or *Anaërobies*.—Names applied by Pasteur to the infusoria which act as ferments only when the air is excluded,—those which require the presence of air to induce their action being distinguished as *Azymiques* or *Aërobies*.

ZYMOME (from ζύμη, yeast, or ferment).—An old name for the portion of gluten which is insoluble in alcohol.

ZYMOSCOPE. An instrument contrived by Zenneck (Buchn. Repert. lix. 204), for testing the fermenting power of yeast, by bringing it in contact with sugar-water, and observing the quantity of carbonic anhydride evolved.

ZYMURGY. A name applied to that department of technological chemistry which treats of the scientific principles of wine-making, brewing, distilling, and the preparation of yeast and vinegar,—processes in which fermentation plays the principal part.

ADDITIONS AND CORRECTIONS.

ACETANILIDE. *Phenylacetamide*, $C^8H^9NO = NH(C^6H^5)(C^2H^3O)$, is easily produced by cohobating aniline with strong acetic acid, or by boiling the two together, and finally distilling till the product solidifies in the neck of the retort (C. Gr. Williams, Chem. Soc. J. xvii. 106). According to Perkin's observation, crude aniline, prepared by Béchamp's process with an excess of strong acetic acid, sometimes contains acetanilide. According to Lauth (Bull. Soc. Chim. 1866, i. 164), acetanilide is produced, together with phenol, by boiling equal parts of aniline and phenylic acetate in a flask with vertical condensing-tube, or by heating them in a closed vessel to 250°:

$$C^2H^3O.C^6H^5.O + NH^2(C^6H^5) = C^6H^5.H.O + NH(C^6H^5)(C^2H^3O).$$

The phenol and acetanilide are easily separated by distillation, or by treatment with an alkali.

Acetanilide has a specific gravity of 1·099 at 105°, melts at 101°, and distils at 295° under a pressure of 755 mm. Vapour-density, obs. = 4·847; calc. = 4·671. Acetanilide dissolves easily in alcohol, ether, benzene, and volatile oils, and crystallises from the latter in large needles. The alcoholic solution is not precipitated by water. It dissolves easily in warm sulphuric and hydrochloric acids, and is converted, by cold nitric acid, into β-nitraniline. When heated with sodium, it is resolved into aniline, and a small quantity of basic oil having a high boiling-point. (Williams.)

AGE, or AXIN. A fat obtained in Mexico by boiling a species of coccus (*Coccus Axin*) with water. It smells like arnica-flowers, has a dark-brown colour, and buttery consistence; hardens on exposure to the air, and dries up on the skin to an adhesive elastic membrane, like collodion: hence it is used by the Mexicans as an external application, and frequently as a varnish. It is insoluble in water, dissolves with difficulty in cold, more readily in hot alcohol, easily in ether, provided it has not been hardened and oxidised by exposure to the air. Melts at 31°; gives off acrolein by dry distillation. The saponified fat yields a crystallisable acid, melting at 42°, and having the composition of lauric acid, $C^{12}H^{24}O^2$; together with a brown oily acid, called axinic acid, which solidifies somewhat above 0°, dries up very easily, and probably contains $C^{18}H^{28}O^2$. This acid is converted, by oxidation, partly into hypogæic acid, $C^{16}H^{30}O^2$ (soluble in alcohol and ether, and melting at 35°); partly into aginin, an amorphous, light-yellow, brittle substance, insoluble in water, alcohol, and ether, and containing 58·3 to 60·3 per cent. carbon, and 6·7 to 7·5 per cent. hydrogen; it turns brown at 80°, giving off water and colourless gases absorbable by potash. (Hoppe, J. pr. Chem. xxx. 102; Gm. xvii. 46.)

AGININ. See the previous article.

ALCOGEL. }
ALCOSOL. } See COLLOÏDAL ACIDS (p. 1088).

ALOÏN. This substance, the purgative principle of aloes, was discovered by T. and H. Smith (Chem. Gaz. 1851, p. 107; Gm. xvi. 461).

ARIBINE. $C^{23}H^{20}N^4$. (Rieth and Wöhler, Ann. Ch. Pharm. cxx. 247; Jahresb. 1861, p. 532; Gm. xvii. 561.)—A base extracted from the bark of *Arariba rubra*, a Brazilian tree, by exhaustion with water containing sulphuric acid. It may be freed from colouring-matter and other impurities, by treatment with acetate of lead and solution in ether, and separates from the ethereal solution partly in anhydrous rhombic pyramids, partly in hydrated four-sided prisms with oblique end-faces; the latter contain $C^{23}H^{20}N^4.8H^2O$, and give off their water at 100°. Aribine dissolves in 7,762 pts. of water at 23°, more freely in hot water, easily in alcohol, less easily in ether. Its salts are mostly crystallisable, and contain 2 or 4 atoms of acid to 1 atom of base.

—The *hydrochlorate*, $C^{23}H^{20}N^4.2HCl$, crystallises in slender needles, soluble in amylic alcohol, insoluble in ether; from its dilute aqueous solution, caustic soda, sodium-carbonate, ammonia, and lime-water throw down crystalline aribine.—The *chloroplatinate*, $C^{23}H^{20}N^4.2HCl.PtCl^4$, is precipitated in pale-yellow needles.—The *neutral sulphate*, $C^{21}H^{20}N^4.H^2SO^4$, is obtained by decomposing the hydrochlorate with sulphate of silver.—The *acid sulphate*, $C^{23}H^{20}N^4.2H^2SO^4$, is formed by treating aribine with excess of sulphuric acid.

Aribine, heated with iodide of ethyl, forms yellow crystals, probably consisting of iodide of diethyl-aribine, $C^{23}H^{18}(C^2H^5)^2N^4I^2$, which, when decomposed with moist silver-oxide, yields the corresponding hydrate as an amorphous coloured varnish.

ATOMICITY. See CLASSIFICATION (i. 1008—1017).

AXIN. Syn. with AGE (p. 1087).

AXINIC ACID. See AGE (p. 1087).

BENZHYDROL. $C^{13}H^{12}O = C^{13}H^{11}.H.O$.—A monatomic alcohol, produced by the action of nascent hydrogen on benzophenone or phenyl-benzoyl, $C^{13}H^{10}O$, and described in connection with the latter (iv. 478).

BERBERINE. $C^{20}H^{17}NO^4$.—This formula has been established by Perrins (Chem. Soc. Qu. J. xv. 339), by the analysis of the alkaloïd and several of its salts. Berberine is very widely diffused in the vegetable kingdom. Besides the sources of it mentioned in vol. i. (p. 579), it has been found by Perrins in *Hydrastis canadensis* and *Xanthorrhiza apiifolia*, two North American ranunculaceous plants; in a yellow dye-wood from Upper Assam, called *woodunpar*, probably belonging to the menispermaceous order; in a woody root, called *Raiz de São Joao*, or St. John's-root, from Rio Grande; in the yellow bark of the Pachnelo tree, from Bogota; and in the root of *Coptis Tecta* or *Mahmira*, a ranunculaceous plant of Hindostan and China, highly prized for its tonic properties, and known in the bazaars of India as *Mishmee-bitter*. Lastly, the substance called *xanthopicrite*, discovered in 1826 by Chevallier and Pelletan in the bark of *Xanthoxylon Clava Herculis*, has been shown by Perrins to be identical with berberine.

When a dilute solution of iodine in iodide of potassium is added to the solution of any berberine-salt in hot spirit, carefully avoiding an excess of iodine, a crystalline iodine-compound is deposited, in green spangles resembling sulphate of iodoquinine (v. 25), and, like that substance, possessing the power of polarising light. (Perrins.)

BRAZIL-WOOD. (i. 656.)—Preisser's statements respecting the red colouring-matter of this wood are not to be depended upon.

CAMPHRETIC ACID. $C^{10}H^{14}O^7 = \left.\begin{matrix}(C^{10}H^{11}O^4)'''\\ H^3\end{matrix}\right\}O^3$.—A tribasic acid produced by the action of nitric acid upon camphor;—described under PYROCAMPHRETIC ACID (iv. 757).

CESPITINE. $C^8H^{13}N$.—This name is given by Church and Owen (Phil. Mag. [4], xx. 110; Jahresb. 1860, p. 358) to an organic base, found in small quantity, together with pyridine, picoline, collidine, and lutidine, in the liquid obtained by distilling Irish peat at the lowest possible temperature. When purified by fractional distillation, treatment with potash, &c., it forms a colourless oil, miscible in all proportions with water, and agreeing in composition and boiling-point (95°) with amylamine.

CHIMOPHYLLIN. A yellow crystalline body obtained from *Pyrola* (or *Chemophila*) *umbellata* (iv. 760).

CHRYSINIC ACID. A yellow colouring-matter contained in the buds of *Populus nigra* and *P. pyramidalis* (iv. 688).

COLLOÏDAL ACIDS. (Graham, Chem. Soc. J. xvii. 218.)—Colloïdal substances can exist in two states—the liquid state, in which they are soluble in water in all proportions; and the gelatinous or pectous state, in which they are but sparingly soluble. The soluble hydrate of a colloïd substance is called a hydrosol, the gelatinous hydrate a hydrogel. The solubility of a hydrogel diminishes with the quantity of water contained in it. Gelatinous silicic acid containing 1 per cent. of anhydrous silica, dissolves in 5,000 pts. of water; a jelly containing 5 per cent. silica, dissolves in 10,000 pts of water; and anhydrous silica itself is nearly insoluble. The passage from the liquid to the gelatinous state is indicated by a gradual thickening of the solution, which assumes an oily consistence just before gelatinising. In a solution of silicic acid obtained by dialysis (p. 141), the tendency to pass into the gelatinous state increases with the temperature and the concentration of the liquid. A solution containing from 10 to 12 per cent. silica gelatinises in a few hours; a solution containing only 5 per cent. may be kept unaltered for several days; one containing 2 per cent. for many months; another containing 1 per cent. silica remains unaltered for years; and solutions containing only 0·1 per cent. are doubtless quite permanent.

The coagulation of the hydrosol of silicic acid is promoted by small quantities of salts, and, on the other hand, the hydrogel is reconverted into the hydrosol by very small quantities of alkali. One part of sodium-hydrate dissolved in 10,000 pts. of water, gradually liquefies, at 100°, a quantity of gelatinous silicic acid corresponding to 200 pts. of dry silica, and may be separated from the resulting silicious solution by prolonged dialysis in a vacuum.

Silica may be separated both from the hydrosol and the hydrogel by a number of substances, both colloïd and crystalloïd (sulphuric, hydrochloric, nitric, and acetic acids, alcohol, glycerin, sugar-syrup, and other bodies which do not induce gelatinisation), these substances then taking the place of the silica.

The liquid compound of silicic acid with alcohol is called the alcosol, and the gelatinous compound the alcogel of silicic acid. The former produces a nearly colourless solution, which is not gelatinised by salts or by insoluble substances, or even by heating to the boiling-point, but easily gelatinises when concentrated by slow evaporation. Although the alcohol in this compound is less strongly combined than the water in the hydrosol, part of it nevertheless remains behind on distillation, and is ultimately carbonised.

The alcogel of silicic acid is easily prepared by placing masses of gelatinous silica (containing 8 to 10 per cent. SiO^2) in absolute alcohol, and changing the latter repeatedly till the water of the hydrogel is completely replaced by alcohol. An alcogel thus prepared from a hydrogel containing 9·35 per cent., yielded by analysis 88·13 per cent. alcohol, 0·23 water, and 11·64 SiO^2. When immersed in water, the alcogel is gradually reconverted into the hydrogel. By treating the alcogel with ether, benzene, carbonic disulphide, and generally with liquids which mix with alcohol, compounds of silicic acid with these several substances may be obtained; from the ether-compound, in like manner, compounds with fixed oils may be produced.

A glycerogel of silicic acid is obtained by heating the hydrogel with glycerin. It is a perfectly colourless jelly, and so transparent that it cannot be perceived in the liquid. Part of the silica is, at the same time, converted into a liquid compound, the glycerosol of silicic acid. The glycerogel (prepared from a hydrate containing 9·35 per cent. silica) was found to contain 87·44 per cent. glycerin, 3·78 water, and 8·95 SiO^2.

When the hydrogel of silicic acid is immersed, first in moderately dilute sulphuric acid, then successively in stronger acids, and finally in the most concentrated acid (hydric sulphate, H^2SO^4), a gelatinous sulphuric acid compound is obtained, the sulphagel of silicic acid. It is colourless, transparent, of somewhat smaller bulk than the hydrogel, from which it has been prepared; is not altered by heating to the boiling-point of sulphuric acid, but gives up part of its sulphuric acid at a higher temperature. By dialysation with water, it is reconverted into hydrogel; by alcohol into alcogel. Similar compounds may be formed with hydric nitrate, acetate, and formate.

Liquid stannic acid is obtained by dialysing stannic chloride mixed with caustic alkali, or sodic stannate mixed with hydrochloric acid. In both cases a jelly is first formed, which, as the salts are gradually removed, is reconverted into the soluble modification by the small quantity of free alkali present: the latter is removed by prolonged diffusion, most readily after addition of a few drops of iodine-solution. Liquid stannic acid is converted by heat into liquid metastannic acid. Both solutions are easily gelatinised by small quantities of hydrochloric acid or of salts; and, on the other hand, gelatinous stannic acid is reconverted into the liquid acid by free alkali, even at ordinary temperatures.

A solution of gelatinous titanic acid in hydrochloric acid, prepared in the cold, and containing only 1 per cent. SiO^2, yields, in like manner, liquid titanic acid. By heating liquid stannic and titanic acids with alcohol and other liquids, compounds are formed analogous to those obtained in like manner with silicic acid.

Liquid tungstic (or rather metatungstic) acid has been already described (p. 911). A mixture of liquid tungstic and silicic acids does not gelatinise, probably in consequence of the formation of silico-tungstic acids (p. 915).

Liquid molybdic acid is obtained, by dialysing a solution of crystallised sodic molybdate supersaturated with hydrochloric acid, for several days, as a yellow liquid having an astringent taste and acid reaction. It is very permanent, and when left to evaporate, yields soluble molybdic acid as a deliquescent gummy mass, which, when heated, behaves like soluble tungstic acid. Soluble tungstic and molybdic acids yield crystallisable salts by digestion with soda.

CONARITE. A green crystalline mineral, resembling vivianite in structure, found at Röttis, near Jacketa, in the Saxon Voigtland. Specific gravity = 2·46. It appears to be a hydrated nickel-phosphate. (Breithaupt, Jahresb. 1859, p. 806.)

CORIAMYRTIN. $C^{30}H^{36}O^{10}$. (Riban, Bull. Soc. Chim. 1864, i. 87; 1867, i. 79; Laboratory, i. 324.)—The active principle of *Coriaria myrtifolia*, a purgative and very poisonous plant growing in the South of France, in Spain, and in Italy—formerly used for the production of a black dye, and for adulterating senna. Coriamyrtin may be extracted from the berries or the leaves, but the young shoots gathered in March yield the largest product. They are crushed in a mill, and pressed; the juice is treated with basic acetate of lead; and the filtered liquid is freed from excess of lead by sulphydric acid, then evaporated to a syrup, and repeatedly shaken up with ether, which dissolves the coriamyrtin, and leaves it on evaporation in slightly brown crystals, which may be rendered perfectly white and pure by one or two crystallisations from boiling alcohol.

Coriamyrtin is a white, bitter, very poisonous substance, crystallising in oblique rhomboïdal prisms of 98° 40′, having the basal edges truncated. It is anhydrous, and melts at 220° to a colourless liquid, which solidifies to a crystalline mass on cooling. It is slightly soluble in water, easily soluble in boiling alcohol and ether. The alcoholic solution turns the plane of polarisation to the right: $[\alpha] = 24{\cdot}5$ at 20°.

Coriamyrtin is decomposed by fuming hydriodic acid, slowly in the cold, rapidly at 100°, a large quantity of iodine being separated, and a black soft substance deposited; and if the supernatant liquid be decanted, the black substance washed with cold water and dissolved in absolute alcohol, and the resulting solution mixed with a few drops of strong caustic *soda*, a fine purple-red colour is produced, resembling that of an alcoholic solution of fuchsine. This reaction is extremely delicate.

Bromocoriamyrtin, $C^{30}H^{34}Br^2O^{10}$, is formed by adding bromine, drop by drop, to coriamyrtin suspended in cold alcohol. It crystallises from boiling alcohol, in fine anhydrous needles, slightly soluble in cold water, very soluble in boiling alcohol, and having an extremely bitter taste.

Chlorine passed through a mixture of coriamyrtin and water, forms a crystalline substance, composed of several amorphous chlorinated compounds, which cannot be separated by successive crystallisation.

Action of Bases on Coriamyrtin.—Most bases attack coriamyrtin in presence of water. With potash and soda only brown compounds are obtained; but with less active bases, such as baryta and lime, coriamyrtin assumes the elements of five molecules of water, producing a dibasic acid, which unites with the base. Thus, when boiled with excess of baryta, it forms the compound, $C^{30}H^{46}Ba''O^{16} = C^{30}H^{36}O^{10}.BaO.5H^2O$; and with lime-water, in like manner, the salt $C^{30}H^{46}Ca''O^{16}$. These salts do not possess the bitter taste of coriamyrtin.

The acid, separated from them by sulphuric or oxalic acid, remains on evaporation as an amorphous mass. Its aqueous solution decomposes the carbonates of barium and calcium, with effervescence, reproducing the salts just described.

Action of Acids.—Coriamyrtin is dissolved and blackened by strong *sulphuric acid.*—With *fuming nitric acid*, it forms an amorphous nitro-compound, which detonates when heated. It is not attacked by dry *hydrochloric acid gas*, even at 100°, but decomposes when heated to 200° with the aqueous acid containing 2 or 3 per cent. of that gas.

Acetic anhydride and coriamyrtin, heated together to 140° in a sealed tube for about an hour, unite directly without elimination of water. The soft mass thus produced, if thrown into water to free it from acetic acid, ultimately falls to a powder, which may be washed with cold water, then dissolved in alcohol, separated by evaporation, and dried at 100° in a vacuum. It is transparent, nearly colourless, brittle, very bitter, melts below 100°, is insoluble in water, but soluble in alcohol. It has the composition $C^{42}H^{54}O^{19}$, which is that of hexacetic coriamyrtin combined with 3 at. water. Its formation is represented by the equation:

$$C^{30}H^{36}O^{10} + 3(C^2H^3O)^2O = C^{30}H^{30}(C^2H^3O)^6O^{10} + 3H^2O.$$

Glacial acetic acid forms a similar compound with coriamyrtin.

DECYL, RUTYL, CAPRYL. $C^{10}H^{21}$.—The tenth of the series of alcohol-radicles, C^nH^{2n+1}. It has not been isolated.

Hydride of Decyl, $C^{10}H^{22}$ (isomeric with free amyl), is contained in considerable quantity in the portion of American petroleum boiling between 158° and 163° (Pelouze and Cahours, Ann. Ch. Phys. [4], i. 5; Jahresb. 1863, pp. 526, 529).—It is produced also by carefully mixing diamylene, $C^{10}H^{20}$, with bromine, keeping the mixture cool, washing the product with dilute potash, and drying it, then heating it under diminished pressure, and submitting it to fractional distillation (Wurtz, Bull. Soc. Chim. 1863, p. 300; Jahresb. 1863, p. 510). This hydrocarbon resembles amyl in many of its properties (Wurtz). It has an odour of lemons. Specific gravity = 0·757 at 16° (Pelouze and Cahours); 0·753 at 0° (Wurtz). Boiling-point

158°—162° (Pelouze and Cahours); 155°—157° (Wurtz). Vapour-density, obs. = 5·040 (Pelouze and Cahours); 5·05 (Wurtz); calc. = 4·91.

Chloride of Decyl, $C^{10}H^{21}Cl$, obtained from the hydride by the action of chlorine, is a liquid of a light amber colour, boiling at 200°—204° (Pelouze and Cahours); 190°—200° (Wurtz). With alcoholic potash, it yields, amongst other products, a hydrocarbon, which boils between 158° and 160°, and forms a heavy oil with bromine. (Pelouze and Cahours.)

ERUCADIC ACID. $C^{22}H^{42}O^2$.—An acid isomeric with erucic acid (ii. 501), and bearing the same relation to it that elaïdic acid bears to oleic acid. It is produced by the action of nitrous acid gas on erucic acid, and when recrystallised from alcohol, forms a white, inodorous, and tasteless mass, melting at 59° to 60°, and solidifying at 58° to 59° to a shining mass of fine needles. It becomes coloured and odorous at 120°. Its sodium-salt, prepared like that of erucic acid, becomes coloured at 110°. (Websky, J. pr. Chem. lviii. 459.)

ESERINE. Syn. with PHYSOSTIGMINE (iv. 635).

EUGETIC ACID. See Addenda to vol. ii. p. 968.

GLYCEROGEL.
GLYCEROSOL. See COLLOÏDAL ACIDS (p. 1089).

GURJUN-BALSAM. Syn. with WOOD-OIL (v. 1045).

GURJUNIC ACID. The resin left on distilling off the volatile oil of gurjun-balsam.

HYDROGEL.
HYDROSOL. See COLLOÏDAL ACIDS (p. 1088).

HYGROMETRY. (iii. 232).—The formula for calculating the weight of a cubic foot of air, saturated with aqueous vapour, should be:

$$\text{(Weight of cubic foot of dry air)} \,.\, \frac{p-E_t}{p} + \text{Weight of cubic foot of vapour.}$$

When the air is not saturated, if E_d be the elastic force of the vapour at the dew-point, and E_d the elastic force of the vapour at the temperature of the air, then:

$$\text{(Weight of cub. ft. of dry air at } t^\circ) \,.\, \frac{p-E_d}{p} + \text{(Weight of cub. ft. of vapour at } t^\circ) \,.\, \frac{E_d}{E_t}$$

= Weight of cubic feet of moist air not saturated.

This latter formula may be deduced from the formula given on p. 232, vol. iii., for the weight of a cubic foot of non-saturated air, by substituting therein the value of the weight of air saturated with aqueous vapour, determined according to the corrected formula above given.*

ISODULCITE. $C^6H^{14}O^6 = C^6H^{12}O^5.H^2O$.—This saccharine substance, produced by the decomposition of quercitrin (p. 7) under the influence of acids, is isomeric with mannite and dulcite. It crystallises very easily, in large, transparent, regularly-developed crystals, resembling those of cane-sugar: they are hard, grate between the teeth, taste sweeter than grape-sugar, dissolve in 2·09 pts. water at 18°, and easily in absolute alcohol. The solution is dextrorotatory. Isodulcite is not fermentable. It melts, with loss of water, between 105° and 110°, is coloured yellow to brown by strong sulphuric acid, and by alkalis, and reduces cupric oxide. 1,000 c.c. of a copper-solution, equivalent to 5 grms. grape-sugar, are reduced by 5·288 grms. isodulcite.

Isodulcite, heated with hydriodic acid (or with iodine and phosphorus), is converted into a black mass, and yields a small quantity of an oily volatile iodine-compound. By oxidation with nitric acid, it yields an acid resembling saccharic acid, with traces of oxalic acid.

Nitro-isodulcite, $C^6H^9(NO^2)^3O^5$, separates from a solution of isodulcite in a mixture of nitric and sulphuric acids, as a white uncrystallisable body, insoluble in water, but very soluble in alcohol; it explodes slightly by heat, and by percussion. (Hlasiwetz and Pfaundles, Ann. Ch. Pharm. cxxvii. 362.)

LASERPITIN. $C^{24}H^{36}O^7$. (Feldmann, Ann. Ch. Pharm. cxxxv. 336; Bull. Soc. Chim. 1866, i. 457.)—A bitter principle contained in the root of *Laserpitium latifolium*, and exhibiting considerable analogy to those which are extracted from *Athamanta*, *Peucedanum*, *Imperatoria*, and other plants of the composite order. It is extracted by macerating the root with strong alcohol, and when purified from an adhering resin by means of acetate of lead, crystallises in colourless rhombohedral prisms. It is tasteless and inodorous when pure; insoluble in water even at the boiling heat; soluble in benzene, oil of turpentine, and especially in chloroform; soluble also in ether and in carbonic disulphide. It melts at 114°, and solidifies on cooling to a resinous mass, which gradually becomes crystalline. When heated in a tube, it sublimes in oily drops. The alcoholic solution is precipitated by water.

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* For these corrections I am indebted to the kindness of Mr. P. W. Latham, of Cambridge.—H. W.

Laserpitin is insoluble in dilute acids and alkalis. Strong nitric and sulphuric acids dissolve it, but the solutions are precipitated by water. The alcoholic solution is not precipitated by an alcoholic solution of mercuric chloride, lead-acetate, silver-nitrate, or potassium-iodide. Heated in sealed tubes to 150° with strong hydrochloric acid, or to 200° with dilute sulphuric acid, it yields a black pitchy mass.

By the action of concentrated alcoholic potash, laserpitin is resolved into angelic acid and laserol, $C^{14}H^{22}O^4$, a crystalline resin precipitable by sulphuric acid:

$$\underset{\text{Laserpitin.}}{C^{24}H^{36}O^7} + H^2O = \underset{\text{Laserol.}}{C^{14}H^{22}O^4} + \underset{\text{Angelic acid.}}{2C^5H^8O^2},$$

the decomposition being analogous to that of athamantin (i. 430) into oreoselin and valeric acid:

$$\underset{\text{Athamantin.}}{C^{24}H^{30}O^7} + H^2O = \underset{\text{Oreoselin.}}{C^{14}H^{12}O^4} + \underset{\text{Valeric acid.}}{2C^5H^{10}O^2}.$$

The root of *Laserpitium latifolium* yields, by distillation with water, a small quantity of a volatile oil, similar in taste and odour to oil of pelargonium. This oil does not yield angelic acid by oxidation.

LITHOFELLIC ACID. $C^{20}H^{36}O^4$. (Göbel, Ann. Ch. Pharm. xxxix. 237.—Ettling, *ibid.* xxxix. 242.—Wöhler, *ibid.* xli. 150.—Heumann, *ibid.* xli. 303.—Malaguti and Sarzeau, Compt. rend. xv. 518.—Gm. xvii. 375.)—A crystalline acid, which forms the chief constituent of some kinds of oriental bezoars (i. 584). To extract it, the bezoars are dissolved in boiling alcohol, and the crystals, which form slowly on cooling the solution and concentrating the mother-liquor, are purified by recrystallisation, with the help of animal charcoal. Or, the bezoars, after being exhausted with water, are treated for 24 hours with cold dilute ammonia; the filtrate is decolorised with animal charcoal; and the lithofellic acid is precipitated by dilute sulphuric acid and washed. The acid precipitated from alkaline solutions requires still to be purified by crystallisation from boiling alcohol.

Lithofellic acid crystallises in very small, clear, rhombic prisms, with oblique end-faces; hard and easily pulverisable. Melts at 204° (Göbel), 205° (Wöhler), and solidifies, when not heated above its melting-point, to an opaque crystalline mass. When heated a few degrees above its melting-point, it solidifies to a clear amorphous glass, which becomes electric when rubbed, and melts at 105° to 110° to a viscid mass. Alcohol poured upon this amorphous acid produces a large number of fine cracks, and the acid, when left in contact with a little alcohol, again becomes crystalline (Wöhler). The acid slowly excites a bitter taste in the mouth (Winckler). It dissolves in 29 pts. of alcohol at 20°, and in 6½ pts. of boiling alcohol; the solution has an acid reaction. The acid dissolves in 444 pts. of ether at 20°, and in 47 pts. of boiling ether.

Lithofellic acid, when melted in contact with the air, volatilises in white vapours, which exhale an aromatic odour. By dry distillation it loses 1 at. water, and is converted into an acid oil, $C^{20}H^{34}O^3$, called pyrolithofellic acid. Lithofellic acid dissolves in strong sulphuric acid, forming a solution which becomes milky on addition of water. Hot nitric acid converts it into a yellow acid, soluble in acetic acid, crystallising therefrom, and containing $C^{20}H^{28}(NO^2)^2O^8$. (Malaguti and Sarzeau.)

Lithofellic acid, heated with sugar and sulphuric acid, produces a violet coloration similar to that which is produced in like manner by the biliary acids.

The lithofellates are but little known. The acid dissolves easily in caustic alkalis and alkaline carbonates.—The *ammonium-salt* is known only in solution.—The *potassium-* and *ammonium-salts* are amorphous and gummy.—The *barium-salt* forms crystals very soluble in alcohol.—A *lead-salt*, of variable composition, is obtained as a white precipitate, slightly soluble in water, somewhat more soluble in alcohol, on mixing an alcoholic solution of the acid containing a little ammonia, with neutral acetate of lead.—The *silver-salt*, obtained in like manner by precipitation, appears to contain $C^{20}H^{35}AgO^4$.

MACLURIN. Syn. with MORINTANNIC ACID (iii. 1049).

METAPURPURATES. See PURPURATES (iv. 748).

MUCONIC ACID. $C^6H^6O^4$. (F. Bode, Ann. Ch. Pharm. cxxxii. 95; Jahresb. 1864, p. 400.)—A dibasic acid produced by the action of sodium-amalgam on the chlorinated acid, $C^6H^4Cl^2O^4$, obtained by treating mucic acid with pentachloride of phosphorus (iii. 1058). On treating the resulting mass with hydrochloric acid, evaporating to dryness, and exhausting with ether, a solution is obtained, which yields muconic acid as a white laminar mass, melting at 195°, solidifying at 185°, easily soluble in alcohol, sparingly in ether, soluble in 110 pts. of water at 16°, and crystallising from hot water in long prisms, often grouped in stars.

The muconates are for the most part easily soluble and amorphous; the ammonium-salt (but not the free acid) gives a reddish precipitate with ferric chloride, and, if not too dilute, a white precipitate with silver-nitrate.—The *neutral zinc-salt*, $C^6H^4Zn''O^4$, separates from hot water as a white amorphous mass. The *ethylic ether* is a colourless liquid which sinks in water.

NAPHTHYL-COMPOUNDS. *Nitrate of Diazonaphthalene*, $C^{10}H^6N^2.NHO^3$, is formed by the action of nitrous acid on moistened nitrate of naphthylamine, and is obtained, by spontaneous evaporation of the aqueous solution filtered from a brown-red amorphous product, in white, easily soluble, explosive needles.—*Perbromide of Diazonaphthalene*, $C^{10}H^6N^2.HBr^3$, prepared like the corresponding benzene-compound (iv. 431), forms orange-yellow crystals.—The *platinum-salt*, $2(C^{10}H^6N^2.HCl).PtCl^4$, forms short, yellowish, nearly insoluble prisms.—*Diazonaphtholimide*, $C^{10}H^6N^2.HN$, passes over as a yellowish oil when the substance formed by the action of ammonia on the perbromide is distilled with water. It smells like naphthalene, and turns brown in contact with the air.

Naphthyl-hydrate, or *Naphthyl-alcohol*, $C^{10}H^8O = C^{10}H^7.H.O$.—Produced, with evolution of nitrogen, when the aqueous solution of nitrate of diazonaphthalene is boiled:

$$C^{10}H^6N^2 + H^2O = C^{10}H^8O + N^2.$$

When purified by solution in potash, precipitation with acetic acid, and distillation, it forms shining white laminæ, which melt at 91° to a colourless oil. It volatilises without decomposition, burns with a smoky flame; dissolves sparingly in water, easily in alcohol, ether, and benzene; smells like creosote, and has a burning taste. It unites with strong bases, forming easily decomposible compounds; is converted by nitric acid into nitro-compounds, and by bromine into bromonaphthyl-alcohol. (Griess, Chem. Soc. J. xix. 90; Jahresb. 1866, p. 459.)

Naphthylsulphydrate, $C^{10}H^7.H.S$.—Produced by the action of nascent hydrogen (zinc and sulphuric acid) on naphthylsulphurous chloride (p. 561):

$$C^{10}H^7ClSO^2 + 3H^2 = C^{10}H^8S + HCl + 2H^2O.$$

It passes over on distillation as a colourless, strongly refracting oil, having an unpleasant odour, a specific gravity of 1·146 at 23°, boiling without decomposition at 285°, not miscible with water, sparingly soluble in alkalis, easily soluble in alcohol and ether. It acts strongly on finely pulverised mercuric oxide, forming *naphthyl-mercuric sulphide*, $(C^{10}H^7)^2Hg''S^2$, which separates from hot alcohol as a pale-yellow powder.—The corresponding *lead-compound*, $(C^{10}H^7)^2Pb''S^2$, is deposited as a lemon-yellow fusible precipitate, on mixing the alcoholic solutions of lead-acetate and naphthylsulphydrate.—The *copper-compound* is a pale-yellow precipitate.

Naphthyl-disulphide, $(C^{10}H^7)^2S^2$, separates, by spontaneous evaporation from an alcoholic solution of naphthylsulphydrate saturated with ammonia or potash, in yellow monoclinic crystals. It melts at 85°, is insoluble in water, slightly soluble in alcohol, easily in ether. In contact with zinc and sulphuric acid, it is reconverted into naphthylsulphydrate. (Schertel, Ann. Ch. Pharm. cxxxii. 91.)

NITROPOPULIC ACID. Syn. with Dinitrosalicylic acid. (See SALICYLIC ACID, p. 139).

OLEANDRINE. An alkaloïd contained, together with pseudocurarine, in the leaves and branches of the oleander. (See PSEUDOCURARINE, iv. 743.)

PYROLITHOFELLIC ACID. See LITHOFELLIC ACID (p. 1092).

RUTYL. Syn. with DECYL (p. 1090).

SULPHAGEL. See COLLOÏDAL ACIDS (p. 1089).

WEIGHTS AND MEASURES. The weights and measures used in this Dictionary are chiefly those of the French decimal system. The following tables (published by Messrs. De la Rue and Co.) exhibit their equivalents in English weights and measures:—

French Measures of Length.

	In English inches.	In English feet = 12 inches.	In English yards = 3 feet.	In English fathoms = 6 feet.	In English miles = 1760 yards.
Millimetre	0·03937	0·003281	0·0010936	0·0005468	0·0000006
Centimetre	0·39371	0·032809	0·0109363	0·0054682	0·0000062
Decimetre	3·93708	0·328090	0·1093633	0·0546816	0·0000621
Metre	39·37079	3·280899	1·0936331	0·5468165	0·0006214
Decametre	393·70790	32·808992	10·9363306	5·4681653	0·0062138
Hectometre	3937·07900	328·089917	109·3633056	54·6816528	0·0621382
Kilometre	39370·79000	3280·899167	1093·6330556	546·8165278	0·6213824
Myriametre	393707·90000	32808·991667	10936·3305556	5468·1652778	6·2138242

1 Inch = 2·539954 Centimetres.
1 Foot = 3·0479449 Decimetres.

1 Yard = 0·9143835 Metre.
1 Mile = 1·6093149 Kilometre.

French Measures of Surface.

	In English square feet.	In English square yards = 9 square feet.	In English poles = 272·25 square feet.	In English roods = 10890 square feet.	In English acres = 43560 square feet.
Centiare or Square Metre	10·764299	1·196033	0·0395383	0·0009885	0·0002471
Are, or 100 Square Metres	1076·429934	119·603326	3·9538290	0·0988457	0·0247114
Hectare, or 0,000 Square Metres	107642·993419	11960·332602	395·3828959	9·8845724	2·4711431

1 Square Inch = 6·4513669 Square Centimetre.
1 Square Foot = 9·2899683 Square Decimetres.

1 Square Yard = 0·83609715 Square Metre or Centiare.
1 Acre = 0·40467102 Hectare.

French Measures of Capacity.

	In cubic inches.	In cubic feet = 1728 cubic inches.	In pints = 4·65923 cubic inches.	In gallons = 8 pints = 277·27384 cubic inches.	In bushels = 8 gals. = 2218·19075 cubic inches.
Millilitre, or Cubic Centimetre . . .	0·06103	0·000035	0·00176	0·0002201	0·0000275
Centilitre, or 10 Cubic Centimetres . .	0·61027	0·000353	0·01761	0·0022010	0·0002751
Decilitre, or 100 Cubic Centimetres . .	6·10271	0·003532	0·17608	0·0220097	0·0027512
Litre, or Cubic Decimetre . . .	61·02705	0·035317	1·76077	0·2200967	0·0275121
Decalitre, or Centistere	610·27052	0·353166	17·60773	2·2009668	0·2751208
Hectolitre, or Decistere	6102·70515	3·531658	176·07734	22·0096677	2·7512085
Kilolitre, or Stere, or Cubic Metre . .	61027·05152	35·316581	1760·77341	220·0966767	27·5120846
Myrialitre, or Decastere	610270·51519	353·165807	17607·73414	2200·9667675	275·1208459

1 Cubic inch = 16·386176 Cubic Centimetres.
1 Gallon = 4·543458 Litres.

1 Cubic Foot = 28·315312 Cubic Decimetres.

French Measures of Weight.

	In English grains.	In troy ounces = 480 grains.	In avoirdupois lbs. = 7000 grains.	In cwts. = 212 lbs. = 784000 grains.	Tons = 20 cwts. = 15680000 grains.
Milligramme	0·01543	0·000032	0·0000022	0·0000000	0·0000000
Centigramme	0·15432	0·000322	0·0000220	0·0000002	0·0000000
Decigramme	1·54323	0·003215	0·0002205	0·0000020	0·0000001
Gramme	15·43235	0·032151	0·0022046	0·0000197	0·0000010
Decagramme	154·32349	0·321507	0·0220462	0·0001968	0·0000098
Hectogramme	1543·23488	3·215073	0·2204621	0·0019684	0·0000984
Kilogramme	15432·34880	32·150727	2·2046213	0·0196841	0·0009842
Myriagramme	154323·48800	321·507267	22·0462126	0·1968412	0·0098421

1 Grain = 0·064799 Gramme.
1 lb. avd. = 0·453593 Kilogramme.

1 Troy oz. = 31·103496 Grammes.
1 Cwt. = 50·802377 Kilogrammes.

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THE END.

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ERRATA.

The Errata here given for Vols. I., II., *and* III., *apply to the first Edition: many of them have been corrected in Reprints.—The asterisk in the second column indicates that the line is to be counted from the bottom.*

VOL. I.

PAGE	LINE	ERROR	CORRECTION
3	15	u.	and
4	14	und	and
7	35	various,	*dele* comma
9	37	convayed	conveyed
39	20	53	106
—	21	69'.	138
73	17	alcohol	water
74	31	exer	exert
86	12*	Tecknik	Technik
89	8	of	if
90	4*	*n* to the mark *s*	*s* to the mark *n*
114	33	Rocbleder	Rochleder
—	18*	Wolff, u.	Wolff and
122	20*	Furfuramide.	*dele* full stop
149	4	Bonastro	Bonastre
358	15	dimetric	trimetric
449	24*	Cyanate	Cyanide
526	12	Pilley	Tilley
567	33	$C^7H^4OCl^2$	$C^7H^4Cl^2$
646	13*	9 *aq.*	10 *aq.*
648	13	boric acid	borax
651	18*	Ccu	Cu
680	20	Citric	Citraconic
—	23*	Citric acid	Citric and Citraconic acids
708	6	3·6	0·36
—	—	2·06	0·206
—	7	2.	0·2
795	9*	$NaHCO^2$	$NaHCO^3$
923	9*	chlorosalicyl	chlorazosalicyl
993	14	or on this salt	*dele*
—	19	tribromopropionic	dibromopropionic
1011	9*	$(2n-1)$	$-(2n-1)$
1057	3*	pentagonal, dodecahedron	*dele* comma
1089	32*	Ennenite	Euxenite
1096	*fig.* 130	*c*	*b*
—	—	*b*	*c*
—	19*	+6	+9
1099	13*	p. 92	p. 1098

VOL. II.

135	2*	$3H^2O$	$6H^2O$
142	6*	232	234
180	18*	dioxybenzoic	dioxycuminic
190	10	288	228
411	37	$\frac{8P2}{2}$	$\frac{\infty P2}{2}$
467	27	i.	xi.
765	31*	Moneir	Monier
818	12*	diaphragma	diaphragms

ERRATA.

VOL. III.

PAGE	LINE	ERROR	CORRECTION
157	8	34·2	44
167	27, also over cut	fig. 556	556 *a*
178	22* and 26*	sulphocarbonate	sulphocarbamate
—	22*	and the liquid	*dele* and
—	21*	care	and care
181	40	cxxiv.	cxxiv. 289
246	13*	O^{27}	O^{17}
269	17	pp.	ii.
432	12*	value	volume
433	25	$C^3H^5O\ Cu$	$C^3H^5O^2Cu$
—	26	$C^4H^7O\ Cu$	$C^4H^7O^2Cu$
571	8*	537	573
582	29	acid	acids
586	14*	*Cladoniar angiferina*	*Cladonia rangiferina*
598	18	difference	distance
650	17	et	and
749	31	238	938
808	16	p. 800	p. 801
856	10	O^{11}	O''
857	18	contains camphor	contains a camphor
875	14*	melamide	melamine
880	14*	xv.	xv. 24
920	12*	$\left.\begin{matrix}Hhg^2\\H^2\end{matrix}\right\}N$	$\left.\begin{matrix}Hhg^2\\H^2\end{matrix}\right\}N^2$
931	heading of page	Mesotartartaric	Mesotartaric
983	15	chloride	methide
988	29*	do unite	do not unite
1024	23*	142° 20′	142° 7′
1049	14*	35·51	36·51
1050	27*	*opic*	*opii*
1069	36	Myricyl	Myricin

VOL. IV.

PAGE	LINE	ERROR	CORRECTION
52	13	997	967
52	16	6 . 35·5	5 . 35·5
246	35	brown	lower
273	22	first	final
321	5*	$\left.\begin{matrix}H^2\\(C^4H^4O)''\\H\end{matrix}\right\}N$	$\left.\begin{matrix}H^2\\(C^4H^4O)''\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$
389	27	evolved	involved
551	28	diaognal	diagonal
637	35	slate	shale
673	14*	$\left.\begin{matrix}H^{24}\\\overset{iv}{Pt^3}\end{matrix}\right\}\begin{matrix}N^8\\O''\end{matrix}$	$\left.\begin{matrix}H^{24}\\\overset{iv}{Pt^3}\end{matrix}\right\}\begin{matrix}N^6\\R^6\\O''\end{matrix}$
677	13*	diammonio-platinous oxynitrate	tetrammonio-platinous nitrate
718	21	$2H^2O$	$12H^2O$

VOL. V.

PAGE	LINE	ERROR	CORRECTION
210	7	Kelporvarec	Kelp or varec
218	2	of alcohol	*dele* of
398	35	axis	axes
451	11	and	acid
452	9*	malic	maleic
—	8*	maleic	malic
489	20*	$C^8H^{10}SO^3$	$C^{12}H^{10}SO^3$
521	13*	See Sulphuric ethers	s. Ethylene, Sulphate of, ii. 582
528	19*	Atomic weight, 3	Atomic weight, 32
614	13*	potassium	aluminium
615	15	Thornium	Thorinum
—	foot-note	137	231·5
697	5	ammonium	ammonia
701	33 and 42	H^{43}	H^{44}
—	44	Stadeler	Städeler
702	9	volcannic	volcanic
703	last line	Gram, Stehanhouse	Graham, Stenhouse
733	24*	1¼	10¼
867	6*	$\left.\begin{matrix}C^7H^7\\H\end{matrix}\right\}N$	$\left.\begin{matrix}C^7H^7\\H^2\end{matrix}\right\}N$
954	4	silver-nitrate	mercuric nitrate
967	18*	·4041	·3041

C5 Watts, H. 74252
W34 A dictionary of
v.5 chemistry.
1868

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